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AMERICAN LEATHER CHEMISTS ASSOCIATION

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CONTENTS:

Swanie S. Rossander—Obituary - - - - - - - 466

Sampling of Vegetable Tanned Leathers - - - - 466

Methods for Analysis of Vegetable Tanned Leathers - 468

Methods for Analysis of Mineral Tanning Materials 490

Sampling of Mineral Tanned Leathers - - - - 493

Methods for Analysis of Mineral Tanned Leathers - - 495

The Absorption of Ligninsulfonates by Hide Powder
By H. B. MARSHALL, MARY KRIZAN and W. C. HENRY - 505

Effect of Sample Preparation on Precision in the Hide Substance Determination. *By* S. DAHL - - - - 515

Abstracts - - - - - - - - - - - - - - 519

Patents - - - - - - - - - - - - - - 532

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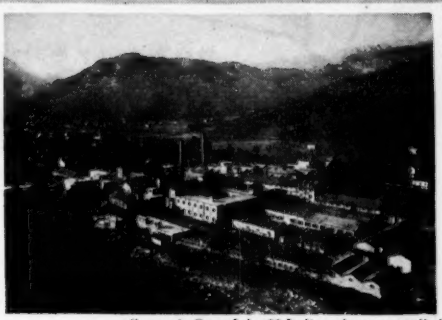

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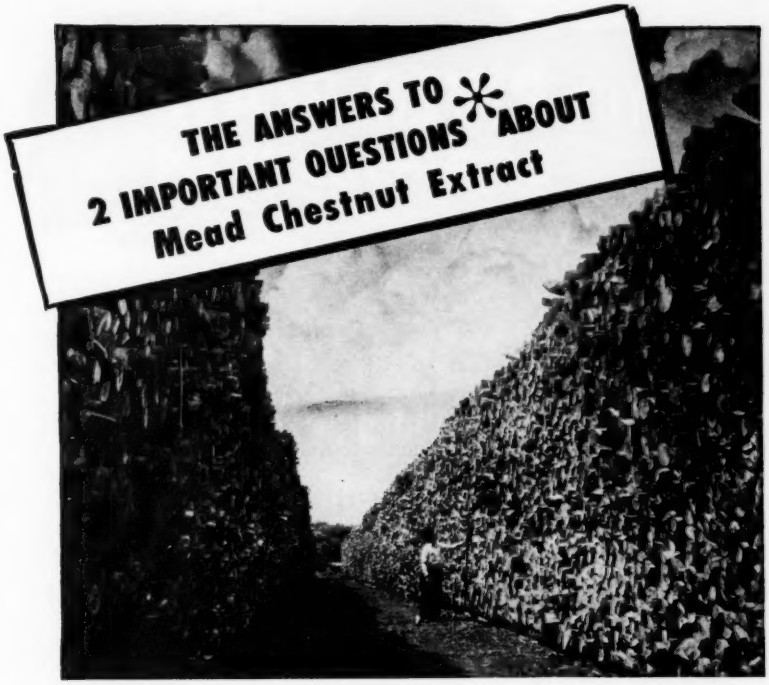

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*** 1. Is the supply of Mead Chestnut Extract adequate?**

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A. Chestnut tanned leathers do not oxidize, darken on exposure to light, or develop an uneven color on aging, as do leathers tanned with many other materials, vegetable or synthetic.

B. Since the tanning system demands acid, the use of chestnut, with its plumping acidity, saves you money.

C. Mead Chestnut Extract eliminates up to 28% of leachhouse losses.

D. There are no hidden costs. When you use Mead Chestnut Extract, no time- and money-consuming preparation is required.

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IT'S A FACT!

Mead Chestnut Extract will produce more pounds of plump leather per unit of tannin than any other tanning material.

Vegetable Tannin	Tan Yard Yield (*white weight basis*)
Chestnut Wood Extract	67%
Tanning Material A	61%
Tanning Material B	63%

Calculate your tanning material costs on a leather basis as well as on a tan unit basis. Mead Chestnut Extract, producing four to six pounds more leather, means positive savings.

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Ask your supplier of tanning materials about Wattle Extract. He will be pleased to offer you the best technical advice on the use of this material for your own particular requirements.

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M.P. . . . . 100°C

Light buff colored solid in flake form. Rapidly soluble in water; slightly soluble in alcohol; insoluble in ether. Also available in solid form.

ANALYSIS

Na_2S	60 to 62%
NaCl	1.5% Max.
Other Na Salts	2.0% Max.
Fe	8 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	35% Min.

SHIPPING CONTAINERS

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SODIUM SULFHYDRATE—NaSH

(sodium hydrosulfide)

Mol. Wt. 56.1
M.P. . . . . 55°C

Light lemon colored solid in flake form. Completely and rapidly soluble in water, alcohol and ether.

ANALYSIS

NaSH	70 to 72%
Na_2S	2.5% Max.
NaCl	0.8% Max.
Na_2SO_3 and $NaHCO_3$	0.4% Max.
Fe	5 ppm Max.
Cu, Ni, Cr, Mn, Pb	1 ppm Max.
Water of crystallization	28 to 26%

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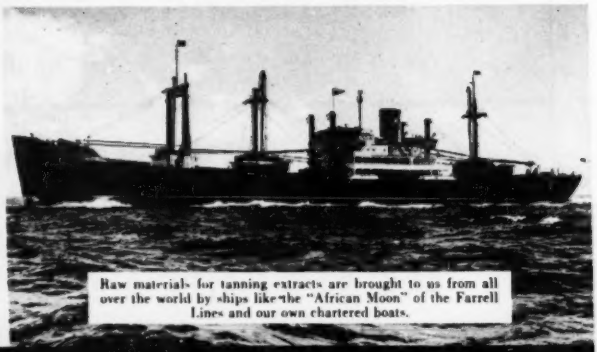

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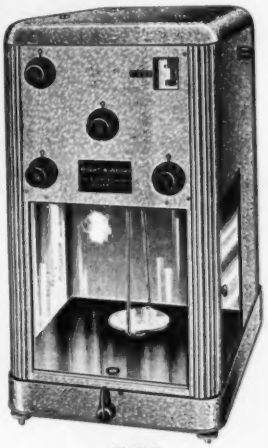

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VOL. XLIX JULY 1954 No. 7

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DR. SWANIE S. ROSSANDER–1904–1954—OBITUARY

Dr. Swanie S. Rossander, Assistant Director of the Jackson Laboratory of the duPont Company, died at his home in Wilmington, Delaware on April the seventeenth. Employed by the duPont Company in 1930, he became Assistant Director of the Jackson Laboratory, in charge of the Analytical Division, Fiber Application Research, Analytical Research and Azo and Hydrophobic Dyes, in 1947. His work brought him into contact with many members of the A.L.C.A. of which he became an active member in 1948.

SAMPLING OF VEGETABLE-TANNED LEATHERS (J15)

The term "Fabricated leather" is used here to designate all products fabricated of vegetable-tanned leather, such as cut soles, straps, belts, welting, packings, bags, cases, gloves, shoes, etc.

The term "Non-frabricated leather" is used here to designate tanned leather pieces, such as hides, skins, sides, crops, backs, bends, bellies, shoulders, etc.

1. SCOPE

1.1 This method is intended for use on all types of vegetable-tanned leather, and on products fabricated therefrom.

2. NUMBER OF PIECES TO BE SAMPLED

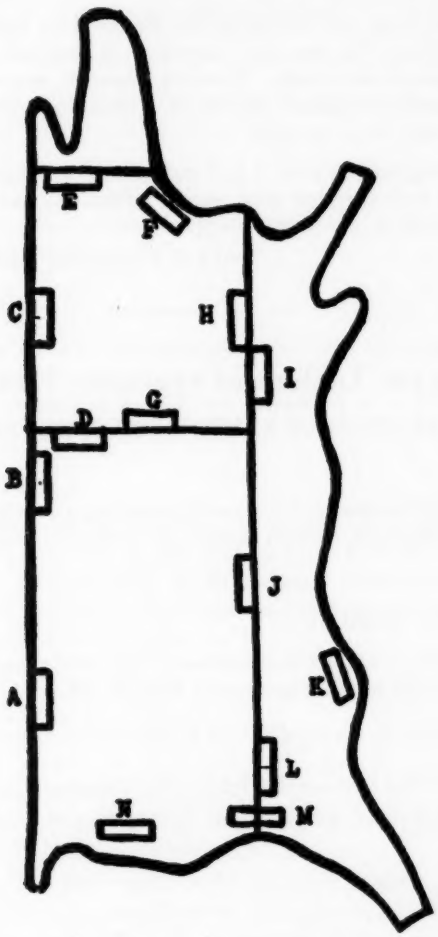
2.1 The number of pieces to be sampled shall be 15 if the lot consists of more than 15 pieces. If there are 15 or fewer pieces in the lot each shall be sample.

2.2 The pieces selected shall be drawn at random, throughout the whole lot of pieces under investigation.

3. LOCATION AND SIZE OF CUTTINGS

3.1 *Fabricated leather.* The cuttings, shall be the pieces themselves, or such portions thereof as it is desired to test.

3.2 *Non-fabricated leather.* Cuttings shall be taken in the relative locations shown in Figure J15. A cutting shall be taken from each prescribed location of each piece of the sample. The center of the cutting shall have the relative location indicated in Figure J15.



Trim	Location
Belly	I—L—K
Single Shoulder	C—H
Sole Leather Bend	A—B—J
Back	A—C—J
Side	A—C—K
Double Shoulder	G—H
Whole Hide	N—F—M
Belting: Butt, Butt Bend or Bend	D

FIGURE J15

3.2.1 Double trims (not shown in the Figure J15) shall be sampled by taking cuttings from the prescribed locations on each side of the backbone line of each piece of the sample. Whenever possible, single bends, butts, or sides shall be sampled because it is difficult to obtain a representative sample from double bends, butts, or sides.

3.2.2 A cutting shall be from 4 to 8 inches long, as required, and 2 inches wide after a 0.5 inch strip has been removed from any untrimmed or uncut edge of the cutting.

ALCA Provisional Method May 1954.

Methods for the Analysis of Vegetable Tanned Leathers

PREPARATION OF SAMPLE FOR ANALYSIS (B1)

1. SCOPE

1.1 This method is intended for use in preparing a representative, composite sample of vegetable tanned leather in a form suitable for chemical analysis.

2. COMPOSITE SAMPLE

2.1 The composite sample shall consist of pieces of equal area from each location and sampled in accordance with Method J15.

3. APPARATUS

3.1 A knife or other tool suitable for cutting leather.

3.2 A Wiley mill fitted with a screen having circular perforations 4 mm. in diameter.

4. PROCEDURE

4.1 Each cutting shall be adjusted so that all cuttings in the sample are of equal area.

4.2 After adjustment, each cutting shall be cut into small pieces with no edge longer than 0.5 inch.

4.3 The small pieces shall be mixed, then ground in the Wiley mill until all material has passed through the screen.

4.4 The ground sample shall be thoroughly mixed then transferred to a bottle and stoppered tightly.

ALCA Provisional Method May 1954.

MOISTURE (B2)

1. SCOPE

1.1 This method is intended for use in determining the moisture in all types of vegetable-tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g. of the sample prepared as directed in Method B1.

3. APPARATUS

3.1 A weighing bottle or moisture dish with a tight cover, and approximately 50 mm. in diameter.

3.2 An oven, electrically heated and controlled, or a Freas Oven as described in Method A13, par. 2.2.

4. PROCEDURE

4.1 The specimen shall be placed in a weighed bottle or dish and the bottle and contents weighed. The bottle, with cover removed, shall be placed in the oven for $16 \pm \frac{1}{4}$ hours with the temperature maintained at $99° \pm 1°$ C. The cover shall be replaced on the bottle, then the bottle shall be transferred to a desiccator, cooled and weighed.

5. RESULTS

5.1 The percentage of moisture in the leather shall be calculated as follows.

$$\text{Moisture, per cent} = \frac{W_2 - W_3}{W_2 - W_1} \times 100$$

where: W_1 = the tare of the dish
W_2 = the weight of the dish plus specimen
W_3 = the weight of the dish plus dried specimen

ALCA Provisional Method May 1954.

PETROLEUM ETHER EXTRACT (B3)

1. SCOPE

1.1 This method is intended for use in determining material extractable by petroleum ether from all types of vegetable-tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g. of the sample prepared as directed in Method B1, except that the amount shall be altered if necessary so that the residue from the petroleum ether extraction does not weigh more than 1 g. nor less than 0.1 g.

3. APPARATUS AND REAGENTS

3.1 An all-glass Soxhlet apparatus consisting of boiling flask, extraction tube and condenser.

3.2 An electric hot plate capable of regulation to give the prescribed boiling rate.

3.3 An extraction thimble, cellulose, fat-free, and fat-free absorbent cotton.

3.4 Petroleum ether boiling between 50° and 80° C.

4. PROCEDURE

4.1 The specimen shall be weighed to the nearest 0.01 g., transferred to the thimble, covered with a pad of cotton, then the thimble shall be placed in the extractor. The extractor boiling flask, which has been dried by heating for 1 hour at 99 ± 1° C., cooled 30 minutes in a desiccator and weighed, shall be connected to the extractor tube. Sufficient petroleum ether shall be added to fill the extractor tube and leave 25–50 ml. in the flask after which the extraction apparatus shall be assembled and heated on the hot plate so that the ether siphons from the tube every 15±3 minutes. The extraction shall continue for at least 5 hours or until all fat has been removed from the leather.

4.2 The apparatus shall be disassembled and the solvent evaporated on a steam bath. Heat shall be applied only until the odor of solvent can no longer be detected (rotation of the flask or a current of air to remove solvent is advisable). Recovery of the solvent by distillation is permissible provided the flask does not go dry. The flask shall be placed in an oven at 99±1° C. for 90 minutes, cooled in a desiccator and weighed.

5. RESULTS

5.1 The percentage of material extractable from the leather by petroleum ether shall be calculated as follows:

$$\text{Material extractable by petroleum ether, percent} = \frac{W_3 - W_2}{W_1} \times 100$$

where: W_1=the weight of the specimen
W_2=the tare of the flask
W_3=the weight of the flask plus dried residue

ALCA Provisional Method May 1954.

CHLOROFORM EXTRACT (B4)

1. SCOPE

1.1 This method is intended for use in determining material extractable by chloroform from all types of vegetable-tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g. of the sample prepared as directed in Method B1, except that the amount shall be altered if necessary so that the residue from the chloroform extraction does not weigh more than 1 g. nor less than 0.1 g.

3. APPARATUS AND REAGENTS

3.1 An all-glass Soxhlet or similar extraction apparatus.

3.2 An A. S. T. M. extractor with metal thimble.

3.3 An electric hot plate capable of regulation to give the prescribed boiling rate.

3.4 An extraction thimble, cellulose, fat-free, and fat-free absorbent cotton.

3.5 Chloroform containing not more than 1 milligram of non-volatile residue per 100 ml.

4. PROCEDURE

4.1 Extraction shall be by either of the following procedures:

4.1.1 The weighed specimen shall be extracted in the Soxhlet extractor and the extract dried and weighed as directed in Method B3, par. 4, except that chloroform shall be used instead of petroleum ether.

4.1.2 The weighed specimen shall be extracted in the ASTM extractor and the extract dried, and weighed as directed in Method B3, par. 4, with the following 3 exceptions: (1) the specimen shall consist of from 3 to 5 g. of the sample, (2) 90 ml. of chloroform shall be used for the extraction, (3) the extraction shall be continued for 2 hours with the heat adjusted so that siphoning occurs about every 2 minutes.

5. RESULTS

5.1 The percentage of material extractable from the leather by chloroform shall be calculated as follows:

$$\text{Material extractable by chloroform, per cent} = \frac{W_3 - W_2}{W_1} \times 100$$

where: W_1 = the weight of the specimen
W_2 = the tare of the flask
W_3 = the weight of the flask plus dried residue

ALCA Provisional Method May 1954.

TOTAL NITROGEN AND HIDE SUBSTANCE (B5)

1. SCOPE

1.1 This method is intended for use in determining the total nitrogen in all types of vegetable-tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of approximately 1.4 g. of the leather sample prepared as directed in Method B1.

3. APPARATUS AND REAGENTS

3.1 Kjeldahl flask, 650 ml. or 800 ml. capacity.

3.2 Boiling chips or other efficient boiling aid.

3.3 Gas or electric heater and flue, aspirator or other means for exhausting fumes generated during the digestion.

3.4 Distillation apparatus consisting of a bulb-trap connected to a vertical water-cooled condenser of block tin, Pyrex glass, or other material which has been shown not to react with hot dilute ammonia solution; the lower end of the condenser shall have an extension tube attached to it which dips into the absorbing agent in a beaker or Erlenmeyer flask. The connection between the trap and condenser shall be so inclined that pools of condensate do not collect therein. All rubber stoppers and connections shall be well seated and gas-tight. The bulb-trap shall be properly baffled to prevent any alkaline spray from being carried over with the liberated ammonia. The Willits-John trap (J. Assoc. Off. Agr. Chemists, **31**, 432-8 (1948)) and the cylindrical type with curved inlet and outlet give good results.

3.5 Sulfuric acid, sp. gr. 1.84, reagent grade, free from nitrogen.

3.6 Sodium hydroxide solution, approximately 11 normal, decanted from any sodium carbonate sludge. (May be prepared by dissolving 450 g. of sodium hydroxide pellets or flakes in water to make 1 liter of solution.)

3.7 Digestion catalyst mixture prepared by grinding together 7 g. of yellow mercuric oxide (reagent grade) and 100 g. of sodium sulfate (anhydrous, free from nitrogen).

3.8 Boric acid indicator solution, 4 per cent solution of reagent grade boric acid free from borates, and containing per liter, 6 ml. of 0.1 per cent solution of methyl red and 4 ml. of 0.1 per cent solution of methylene blue, both made up in 95 per cent ethanol.

3.9 Sodium thiosulfate solution, 80 g. of $Na_2S_2O_3.5H_2O$ per liter of distilled water.

3.10 Standard acid solution, either sulfuric or hydrochloric, approximately 0.3 *N*.

3.11 Sodium hydroxide solution 0.1 *N*, standardized.

4. PROCEDURE

4.1 The specimen shall be weighed to the nearest 0.1 milligram and transferred to the digestion flask. To the flask and leather shall be added 10 g. of the sodium sulfate-mercuric oxide mixture, a few boiling chips, and 25 ml. of concentrated sulfuric acid. The leather, acid and catalyst shall be mixed by shaking, then digested by boiling gently, with the flask inclined, for 1.5 hours total time. The digested material shall be cooled, diluted with 250-300 ml. of distilled water, treated with 8 ml. of the 8 per cent thiosulfate solution, shaken and allowed to stand for at least 10 minutes with occasional shaking.

4.2 Into the receiving vessel of the distillation apparatus shall be measured, with a graduated cylinder, 125 ml. of the boric acid indicator solution, adjusting the receiver so that the outlet of the extension tube from the condenser is immersed.

4.2.1 Instead of boric acid it is permissible to use an accurately measured volume of standardized sulfuric or hydrochloric acid.

4.3 To the digested, diluted material shall be added a few boiling chips and sufficient 11 normal sodium hydroxide solution to make it strongly alkaline. The volume required should be predetermined on a digested blank with litmus paper as indicator. An excess of about 10 ml. should be used; too great an excess causes excessive bumping; usually 95 ml. is adequate. The sodium hydroxide solution should be poured down the side of the flask so that it does not mix with the contents. The flask shall immediately be connected to the distillation trap and the stopper tightly seated. The flask shall be swirled to mix the contents, then heated to distill the liberated am-

monia into the absorbing agent. Distillation shall be continued until all ammonia has been driven over; 150-200 ml. of distillate is generally sufficient. The flask shall be disconnected, the condenser and delivery tube washed down and the distillate diluted, if necessary, to approximately 350 ml. The distillate shall be titrated with the standard acid to the first permanent pink color.

4.4 A blank determination shall be made by the above method, substituting sucrose free from nitrogen for the leather. If the distillate of the blanks be green or gray (the indicator color change, pH about 4.9, is from green to gray to pink), it shall be titrated with standard acid and this volume shall be deducted from the volume of standard acid required by the sample. If the distillate of the blank be pink, sufficient standard alkali shall be added to turn the indicator color green, then the whole shall be titrated with standard acid as described above.

4.4.1 The correction volume (Vo) determined by the following formula shall be added to the volume of standard acid required for the sample.

$$Vo = \frac{V_1 N_1}{N_2} - V_2$$

where Vo = correction volume
V_1 = volume of standard alkali added
V_2 = volume of standard acid used
N_1 = the normality of the standard alkali
N_2 = the normality of the standard acid

5. RESULTS

5.1 *Total Nitrogen.* The total nitrogen in the sample shall be calculated as follows:

$$\text{Total nitrogen, per cent} = \frac{0.014 \times A \times N \times 100}{W}$$

where A = the ml. of standard acid (corrected for blank) required to titrate the specimen
N = the normality of the standard acid
W = the weight of the specimen

5.2 *Hide Substance.* The percentage of hide substance in the leather shall be found by multiplying the percentage of nitrogen by 5.62.

ALCA Provisional Method May 1954.

WATER SOLUBLE MATERIAL (B8)

1. SCOPE

1.1 This method is intended for use in determining the water soluble material in all types of vegetable-tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of 15±.01 g. of the leather sample prepared as directed in Method B1.

2.2 If the leather contains more than 8 per cent of petroleum ether extract on the dry basis, the weighed specimen shall be extracted with petroleum ether boiling between 50° and 80° as directed in Method B3, then left at room temperature until all solvent has evaporated from it.

3. APPARATUS

3.1 A one-liter volumetric flask.

3.2 A Reed-Churchill type extractor (J.A.L.C.A. **14**, 137 (1919)). The extraction tube shall have an internal diameter of 45±2 mm. and a body height of 233±10 mm. The water bath shall be equipped to control the temperature to 35°±0.5° C.

4. PROCEDURE

4.1 The specimen shall be placed in the extraction tube and extracted, at 35° C., at such a rate as to give 1 liter of extract in 3 hours. The extract shall be cooled to 23° C., adjusted to volume, and thoroughly mixed.

4.2 If the extract is clear, 100 ml. shall be pipetted into a tared tannin dish, evaporated and dried in a mechanical convection oven (Method A13), transferred to desiccator, cooled, and weighed.

4.3 If the extract is not clear, it shall be filtered as directed in Method A21. The clear filtrate shall be pipetted, dried, and the residue weighed as directed in par. 4.2 above.

5. RESULTS

5.1 The percentage of water soluble material in the leather shall be calculated as follows:

$$\text{Water soluble material, per cent} = \frac{W_2 - W_1}{W_3} \times 1000$$

where W_1 = tare of the tannin dish
W_2 = weight of tannin dish and residue
W_3 = weight of the leather specimen

ALCA Provisional Method May 1954.

SOLUBLE NON TANNIN AND UNCOMBINED TANNIN (B9)

1. SCOPE

1.1 This method is intended for use in determining the soluble non tannin and uncombined tannin in all types of vegetable tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of 200 ml. of the water soluble solution obtained as directed in Method B8.

3. APPARATUS AND REAGENTS

3.1 The apparatus and reagents shall be as specified in Method A22.

4. PROCEDURE

4.1 The specimen shall be shaken with hide powder, filtered from the hide powder, filtered with Kaolin through paper, evaporated and dried, exactly as directed in Method A22, except that 25 g. of washed hide powder (containing $72.5 \pm 1.5\%$ moisture) shall be used instead of approximately 46 g. (equivalent to 12.5 g. of dry powder) as specified in paragraph 4.3.1 of Method A22.

5. RESULTS

5.1 The percentage of *soluble non tannin* in the leather shall be calculated as follows:

$$\text{Soluble non tannin, per cent} = \frac{F\,(W_2 - W_1)}{W_3} \times 1000$$

where W_1 = tare of the tannin dish
W_2 = weight of the dish and residue
W_3 = the weight of the leather specimen
and F = obtained by adding the g. of water in the 25 g. of wet hide powder used in par. 4.1 to 200 and dividing the sum by 200.

5.2 The percentage of *uncombined tannin* in the leather shall be calculated as follows:

Uncombined tannin, per cent = per cent water soluble material minus per cent soluble non tannin

where per cent water soluble material is determined as in Method B8 and per cent soluble non tannin is determined as in par. 5.1 above.

ALCA Provisional Method May 1954.

GLUCOSE (B10)

1. SCOPE

1.1 This method is intended for use in determining glucose in all types of vegetable-tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of 200 ml. of the water solubles solution obtained as directed in Method B8. It is equivalent to 3 g. of leather.

3. APPARATUS AND REAGENTS

3.1 A filtering crucible, porcelain, fine porosity; or a Gooch-asbestos crucible prepared as follows. Digest finely divided long fibered asbestos with nitric acid (1 to 3) for from 2 to 3 days, wash free from acid and then digest for the same period with 10 per cent sodium hydroxide solution and wash free from alkali. In preparing the Gooch crucible make a bottom layer of about ¼ of an inch with the coarser particles of asbestos and dress off with the fine asbestos. Wash the mat with boiling Fehling's solution, then with nitric acid (1 to 3), and finally with hot water. Crucibles so prepared can be used for a long time.

3.2 A crucible holder and suction flask, with connections to a vacuum.

3.3 A pleated filter paper, C. S. & S. No. 610, 21.5 cm. diameter as specified in Method A21.

3.4 Beakers, 400 ml., low form.

3.5 A saturated solution of normal lead acetate.

3.6 Dipotassium hydrogen phosphate, K_2HPO_4, that has been dried at 100° C. for 16 hours then stored in a tightly stoppered bottle.

3.7 Phenolphthalein solution: 0.5 g. in 100 ml. of 95 per cent alcohol.

3.8 Sodium hydroxide solution prepared as directed in Method B5, par. 3.6, then diluted 1 to 1.

3.9 Stearic acid, powdered.

3.10 Tartaric acid, powdered.

3.11 Copper sulfate solution prepared by dissolving 69.278 g. of $CuSO_4 \cdot 5H_2O$ in 1 liter of water and filtering through asbestos.

3.12 Alkaline tartrate solution prepared by dissolving 346 g. of Rochelle salt and 100 g. of sodium hydroxide in 1 liter of water. After standing for 2 days the solution shall be filtered through asbestos.

4. PROCEDURE

4.1 The 200 ml. specimen shall be pipetted into a 500 ml. Erlenmeyer flask, 25 ml. of saturated lead acetate solution added and the solution shaken fre-

quently for 5 or 10 minutes. The solution shall be filtered, returning the filtrate to the paper until it is clear. During all filtrations the funnel shall be covered. The clear filtrate shall be collected in a flask containing 5.5±1 g. of the dry dipotassium phosphate and shaken frequently. The solution should drain completely from the lead tannate. The lead phosphate shall be filtered from the solution, again with allowance of ample time for all solution to drain from the phosphate. To a 500 ml. Erlenmeyer flask, 150 ml. of the filtrate and 7.5 ml. of concentrated hydrochloric acid (sp. gr. 1.19) shall be added by pipette, also about 25 milligrams of stearic acid. The solution shall be boiled under a reflux condenser for exactly 2 hours to hydrolyze sugars, then left overnight at room temperature. (If foaming occurs just as the solution starts to boil, remove the flame until foaming subsides, then continue the hydrolysis.) The hydrolyzed solution shall be cooled at 12±3° C., treated with 2 drops of phenolphthalein solution, and neutralized with the sodium hydroxide solution with addition of an excess of 0.5 ml. *Without delay*, the solution shall be transferred quantitatively to a 200 ml. volumetric flask, diluted to volume, mixed and filtered until clear. During filtration the clear filtrate shall be kept slightly acid by addition of powdered tartaric acid.

4.2 As soon as the hydrolyzed, neutralized solution has been filtered, a 50-ml. aliquot shall be measured by pipette into a 400 ml. beaker containing a mixture of 25 ml. of the alkaline tartrate solution and 25 ml. of the copper sulfate solution, and the beaker covered. The solution shall be heated to 100°C., as indicated by a thermometer, in exactly 4 minutes and boiling continued for exactly 2 minutes.

4.2.1 The rate of heating should be regulated before the determination is started by adjusting the burner so that 50 ml. of water, 25 ml. of the copper sulfate solution and 25 ml. of the tartrate solution in a 400 ml. beaker will be heated to 100° C. in exactly 4 minutes.

4.3 The solution, without dilution, shall be filtered immediately through the tared crucible, and the residue washed thoroughly with hot water, then with alcohol and finally with ether. The crucible and contents shall be dried for 30 minutes at 99±1° C., cooled in a desiccator and weighed.

5. RESULTS

5.1 From the accompanying Munson and Walker's Table the milligrams of dextrose equivalent to the milligrams of cuprous oxide found shall be determined. The percentage of glucose in the leather shall be calculated as follows:

Glucose, per cent = milligrams of dextrose, determined above multiplied by 200.

MUNSON AND WALKER'S TABLE

(Bulletin 107, Revised, Bureau of Chemistry, page 243).

(Expressed in milligrams).

Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)
10	8.9	4.0	55	48.9	23.5	100	88.8	43.3
11	9.8	4.5	56	49.7	23.9	101	89.7	43.8
12	10.7	4.9	57	50.6	24.3	102	90.6	44.2
13	11.5	5.3	58	51.5	24.8	103	91.5	44.7
14	12.4	5.7	59	52.4	25.2	104	92.4	45.1
15	13.3	6.2	60	53.3	25.6	105	93.3	45.5
16	14.2	6.6	61	54.2	26.1	106	94.2	46.0
17	15.1	7.0	62	55.1	26.5	107	95.0	46.4
18	16.0	7.5	63	56.0	27.0	108	95.9	46.9
19	16.9	7.9	64	56.8	27.4	109	96.8	47.3
20	17.8	8.3	65	57.7	27.8	110	97.7	47.8
21	18.7	8.7	66	58.6	28.3	111	98.6	48.2
22	19.5	9.2	67	59.5	28.7	112	99.5	48.7
23	20.4	9.6	68	60.4	29.2	113	100.4	49.1
24	21.3	10.0	69	61.3	29.6	114	101.3	49.6
25	22.2	10.5	70	62.2	30.0	115	102.2	50.0
26	23.1	10.9	71	63.1	30.5	116	103.0	50.5
27	24.0	11.3	72	64.0	30.9	117	103.9	50.9
28	24.9	11.8	73	64.8	31.4	118	104.8	51.4
29	25.8	12.2	74	65.7	31.8	119	105.7	51.8
30	26.6	12.6	75	66.6	32.2	120	106.6	52.3
31	27.5	13.1	76	67.5	32.7	121	107.5	52.7
32	28.4	13.5	77	68.4	33.1	122	108.4	53.2
33	29.3	13.9	78	69.3	33.6	123	109.3	53.6
34	30.2	14.3	79	70.2	34.0	124	110.1	54.1
35	31.1	14.8	80	71.1	34.4	125	111.0	54.5
36	32.0	15.2	81	71.9	34.9	126	111.9	55.0
37	32.9	15.6	82	72.8	35.3	127	112.8	55.4
38	33.8	16.1	83	73.7	35.8	128	113.7	55.9
39	34.6	16.5	84	74.6	36.2	129	114.6	56.3
40	35.5	16.9	85	75.5	36.7	130	115.5	56.8
41	36.4	17.4	86	76.4	37.1	131	116.4	57.2
42	37.3	17.8	87	77.3	37.5	132	117.3	57.7
43	38.2	18.2	88	78.2	38.0	133	118.1	58.1
44	39.1	18.7	89	79.1	38.4	134	119.0	58.6
45	40.0	19.1	90	79.9	38.9	135	119.9	59.0
46	40.9	19.6	91	80.8	39.3	136	120.8	59.5
47	41.7	20.0	92	81.7	39.8	137	121.7	60.0
48	42.6	20.4	93	82.6	40.2	138	122.6	60.4
49	43.5	20.9	94	83.5	40.6	139	123.5	60.9
50	44.4	21.3	95	84.4	41.1	140	124.4	61.3
51	45.3	21.7	96	85.3	41.5	141	125.2	61.8
52	46.2	22.2	97	86.2	42.0	142	126.1	62.2
53	47.1	22.6	98	87.1	42.4	143	127.0	62.7
54	48.0	23.0	99	87.9	42.9	144	127.9	63.1

MUNSON AND WALKER'S TABLE—(Continued)

Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)
145	128.8	63.6	192	170.5	85.3	239	212.3	107.5
146	129.7	64.0	193	171.4	85.7	240	213.2	108.0
147	130.6	64.5	194	172.3	86.2	241	214.1	108.4
148	131.5	65.0	195	173.2	86.7	242	215.0	108.9
149	132.4	65.4	196	174.1	87.1	243	215.8	109.4
150	133.2	65.9	197	175.0	87.6	244	216.7	109.0
151	134.1	66.3	198	175.9	88.1	245	217.6	110.4
152	135.0	66.8	199	176.8	88.5	246	218.5	110.8
153	135.9	67.2	200	177.7	89.0	247	219.4	111.3
154	136.8	67.7	201	178.5	89.5	248	220.2	111.8
155	137.7	68.2	202	179.4	89.8	249	221.2	112.3
156	138.6	68.6	203	180.3	90.4	250	222.1	112.8
157	139.5	69.1	204	181.2	90.9	251	223.0	113.2
158	140.3	69.5	205	182.1	91.4	252	223.8	113.7
159	141.2	70.0	206	183.0	91.8	253	224.7	114.2
160	142.2	70.4	207	183.9	92.3	254	225.6	114.7
161	143.0	70.9	208	184.8	92.8	255	226.5	115.2
162	143.9	71.4	209	185.6	93.2	256	227.4	115.7
163	144.8	71.8	210	186.5	93.7	257	228.3	116.1
164	145.7	72.3	211	187.4	94.2	258	229.2	116.6
165	146.6	72.8	212	188.3	94.6	259	230.1	117.1
166	147.5	73.2	213	189.2	95.1	260	231.0	117.6
167	148.3	73.7	214	190.1	95.6	261	231.8	118.1
168	149.2	74.1	215	191.0	96.1	262	232.7	118.6
169	150.1	74.6	216	191.9	96.5	263	233.6	119.0
170	151.0	75.1	217	192.8	97.0	264	234.5	119.5
171	151.9	75.5	218	193.6	97.5	265	235.4	120.0
172	152.8	76.0	219	194.5	98.0	266	236.3	120.5
173	153.7	76.4	220	195.4	98.4	267	237.2	121.0
174	154.6	76.9	221	196.3	98.9	268	238.1	121.5
175	155.5	77.4	222	197.2	99.4	269	238.9	122.0
176	156.3	77.8	223	198.1	99.9	270	239.8	122.5
177	157.2	78.3	224	199.0	100.3	271	240.7	122.9
178	158.1	78.8	225	199.9	100.8	272	241.6	123.4
179	159.0	79.2	226	200.7	101.3	273	242.5	123.9
180	159.9	79.7	227	201.6	101.8	274	243.4	124.4
181	160.8	80.1	228	202.5	102.2	275	244.3	124.9
182	161.7	80.6	229	203.4	102.7	276	245.2	125.4
183	162.6	81.1	230	204.3	103.2	277	246.1	125.9
184	163.4	81.5	231	205.2	103.7	278	246.9	126.4
185	164.3	82.0	232	206.1	104.1	279	247.8	126.9
186	165.2	82.5	233	207.0	104.6	280	248.7	127.3
187	166.1	82.9	234	207.9	105.1	281	249.6	127.8
188	167.0	83.4	235	208.7	105.6	282	250.5	128.3
189	167.9	83.9	236	209.6	106.0	283	251.4	128.8
190	168.8	84.3	237	210.5	106.5	284	252.3	129.3
191	169.7	84.8	238	211.4	107.0	285	253.0	129.8

MUNSON AND WALKER'S TABLE—(Continued)

Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)
286	254.0	130.3	333	295.8	153.7	380	337.5	177.9
287	254.9	130.8	334	296.7	154.2	381	338.4	178.4
288	255.8	131.3	335	297.6	154.7	382	339.3	178.9
289	256.7	131.8	336	298.5	155.2	383	340.2	179.4
290	257.6	132.3	337	299.3	155.8	384	341.1	180.0
291	258.5	132.7	338	300.2	156.3	385	342.0	180.5
292	259.4	133.2	339	301.1	156.8	386	342.9	181.0
293	260.3	133.7	340	302.0	157.3	387	343.8	181.5
294	261.2	134.2	341	302.9	157.8	388	344.6	182.0
295	262.0	134.7	342	303.8	158.3	389	345.5	182.6
296	262.9	135.2	343	304.7	158.3	390	346.4	183.1
297	263.8	135.7	344	305.6	159.3	391	347.3	183.6
298	264.7	136.2	345	306.5	159.8	392	348.2	184.1
299	265.6	136.7	346	307.3	160.3	393	349.1	184.7
300	266.5	137.2	347	308.2	160.8	394	350.0	185.2
301	267.4	137.7	348	309.1	161.4	395	350.9	185.7
302	268.3	138.2	349	310.0	161.9	396	351.8	186.2
303	269.1	138.7	350	310.9	162.4	397	352.6	186.8
304	270.0	139.2	351	311.8	162.9	398	353.5	187.3
305	270.9	139.7	352	312.7	163.4	399	354.4	187.8
306	271.8	140.2	353	313.6	163.9	400	355.3	188.4
307	272.7	140.7	354	314.4	164.4	401	356.2	188.9
308	273.6	141.2	355	315.3	164.9	402	357.1	189.4
309	274.5	141.7	356	316.2	165.4	403	358.0	189.9
310	275.4	142.2	357	317.1	166.0	404	358.9	190.5
311	276.3	142.7	358	318.0	166.5	405	359.7	191.0
312	277.1	143.2	359	318.9	167.0	406	360.6	191.5
313	278.0	143.7	360	319.8	167.5	407	361.5	192.1
314	278.9	144.2	361	320.7	168.0	408	362.4	192.6
315	279.8	144.7	362	321.6	168.5	409	363.3	193.1
316	280.7	145.2	363	322.4	169.0	410	364.2	193.7
317	281.6	145.7	364	323.3	169.6	411	365.1	194.2
318	282.5	146.2	365	324.2	170.1	412	366.0	194.7
319	283.4	146.7	366	325.1	170.6	413	366.9	195.2
320	284.2	147.2	367	326.0	171.1	414	367.7	195.8
321	285.1	147.7	368	326.9	171.6	415	368.6	196.3
322	286.0	148.2	369	327.8	172.1	416	369.5	196.8
323	286.9	148.7	370	328.7	172.7	417	370.4	197.4
324	287.8	149.2	371	329.5	173.2	418	371.3	197.9
325	288.7	149.7	372	330.4	173.7	419	372.2	198.4
326	289.6	150.2	373	331.3	174.2	420	373.1	199.0
327	290.5	150.7	374	332.2	174.7	421	374.0	199.5
328	291.4	151.2	375	333.1	175.3	422	374.8	200.1
329	292.2	151.7	376	334.0	175.8	423	375.7	200.6
330	293.1	152.2	377	334.9	176.3	424	376.6	201.1
331	294.0	152.7	378	335.8	176.8	425	377.5	201.7
332	294.9	153.2	379	336.7	177.3	426	378.4	202.2

MUNSON AND WALKER'S TABLE—(Continued)

Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)	Cuprous oxide (Cu_2O)	Copper (Cu)	Dextrose (*d*-glucose)
427	379.3	202.8	449	398.8	214.7	470	417.5	226.2
428	380.2	203.3	450	399.7	215.2	471	418.4	226.8
429	381.1	203.8	451	400.6	215.8	472	419.3	227.4
430	382.0	204.4	452	401.5	216.3	473	420.2	227.9
431	382.8	204.9	453	402.4	216.9	474	421.0	228.5
432	383.7	205.5	454	403.3	217.4	475	421.9	229.0
433	384.6	206.0	455	404.2	218.0	476	422.8	229.6
434	385.5	206.5	456	405.1	218.5	477	423.7	230.1
435	386.4	207.1	457	405.9	219.1	478	424.6	230.7
436	387.3	207.6	458	406.8	219.6	479	425.5	231.3
437	388.2	208.2	459	407.7	220.2	480	426.4	231.8
438	389.1	208.7	460	408.6	220.7	481	427.3	232.4
439	390.0	209.2	461	409.5	221.3	482	428.1	232.9
440	390.8	209.8	462	410.4	221.8	483	429.0	233.5
441	391.7	210.3	463	411.3	222.4	484	429.9	234.1
442	392.6	210.9	464	412.2	222.9	485	430.8	234.6
443	393.5	211.4	465	413.0	223.5	486	431.7	235.2
444	394.4	212.0	466	413.9	224.0	487	432.6	235.7
445	395.3	212.5	467	414.8	224.6	488	433.5	236.3
446	396.2	213.1	468	415.7	225.1	489	434.4	236.9
447	397.1	213.6	469	416.6	225.7	490	435.3	237.4
448	397.9	214.1						

ALCA Provisional Method May 1954.

INSOLUBLE ASH (B11)

1. SCOPE

1.1 This method is intended for use in determining the insoluble ash in all types of vegetable-tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of the leather remaining after water extraction, as directed in Method B8.

3. APPARATUS

3.1 A large porcelain or platinum crucible.

3.2 A muffle furnace with temperature controller or rheostat and pyrometer.

4. PROCEDURE

4.1 The specimen shall be removed quantitatively from the extraction tube, dried, transferred to the crucible, placed in a cold muffle furnace, and ashed at 600±25° C. as directed in Method B15, Total Ash.

5. RESULTS

5.1 The percentage of insoluble ash in the leather shall be calculated as follows.

$$\text{Insoluble ash, per cent} = \frac{W_3 - W_2}{W_1} \times 100$$

where: W_1 = the weight of specimen (15 g.) used in Method B8
W_2 = the tare of the ash dish
W_3 = the weight of the dish plus ash

ALCA Provisional Method May 1954.

COMBINED TANNIN AND DEGREE OF TANNAGE (B12)

1. SCOPE

1.1 This method is intended for use in calculating the percentage of combined tannin and the degree of tannage of all types of vegetable tanned leather.

2. RESULTS

2.1 The percentage of *combined tannin* shall be obtained by subtracting from 100 the sum of the percentages of moisture (Method B2), petroleum ether extract (Method B3), hide substance (Method B5), water soluble matter (Method B8), and Insoluble Ash (Method B11).

2.2 The *degree of tannage* shall be calculated as follows:

$$\text{Degree of tannage} = \frac{A \times 100}{B}$$

where: A = the present combined tannin determined in par. 2.1 above

B = the per cent hide substance determined in Method B5.

ALCA Provisional Method May 1954.

TOTAL ASH (B15)

1. SCOPE

1.1 This method is intended for use in determining the total ash in all types of vegetable-tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of approximately 5 g. of the sample prepared as directed in Method B1.

2.1.1 The dried leather specimen from Method B2 may be used.

3. APPARATUS

3.1 A large porcelain or platinum crucible.

3.2 A muffle furnace with temperature controller or with rheostat and pyrometer.

4. PROCEDURE

4.1 Approximately 5 g. of the sample shall be accurately weighed, transferred to a tared crucible and placed in the cold muffle furnace. (The specimen may be weighed directly in the tared crucible if more convenient.) The temperature of the furnace shall be raised gradually to 600±25° C. and maintained at this temperature until the crucible and contents have reached constant weight. If it is difficult to burn off all carbon, hot water shall be added to the residue and the solution filtered through an ashless filter paper. The paper and residue shall be dried and ignited in the crucible, then the filtrate shall be added to the crucible, evaporated, and the crucible again ignited.

4.1.1 It is sometimes sufficient to moisten the ash, dry, and ignite. The crucible shall then be removed to a desiccator, cooled, and weighed.

5. RESULTS

5.1 The percentage of total ash in the leather shall be calculated as follows:

$$\text{Total Ash, per cent} = \frac{W_3 - W_1}{W_2 - W_1} \times 100$$

where: W_1 = the tare of the dish
W_2 = the weight of dish plus specimen
W_3 = the weight of dish plus ash

ALCA Provisional Method May 1954.

MAGNESIUM AS EPSOM SALTS (B16)

1. SCOPE

1.1 This method is intended for use in determining the magnesium (as Epsom salts) in all types of vegetable-tanned sole leather.

2. SPECIMEN

2.1 The specimen shall consist of the ash of approximately 5 g. of the leather prepared as directed in Method B1.

3. APPARATUS

3.1 A filtering crucible, porcelain, fine porosity; or a Gooch-asbestos crucible.

3.2 A crucible holder and suction flask with connections to vacuum.

3.3 Ammonium hydroxide (sp. gr. 0.90) diluted 1 to 1.

3.4 Ammonium hydroxide (sp. gr. 0.90) diluted 1 to 9.

3.5 Ammonium oxalate, saturated solution.

3.6 Ammonium nitrate, 50 per cent solution in 1:9 ammonium hydroxide.

3.7 Ferric chloride, 10 per cent solution.

3.8 Indicator solution, made by mixing 2 parts of 0.1 per cent methyl red with 1 part of 0.1 per cent methylene blue, both in 95 per cent ethanol.

3.9 Methanol, 60 per cent by volume.

3.10 Sodium ammonium hydrogen phosphate, saturated solution, clear.

4. PROCEDURE

4.1 The specimen in the crucible shall be moistened with water, treated with 15 ml. of concentrated hydrochloric acid and washed into a beaker. The solution shall be diluted to 50–75 ml., treated with 2-3 drops of concentrated nitric acid and heated on a steam bath for about 15 minutes. Ammonium hydroxide, 1 to 1, shall be added to the unfiltered solution, slowly, with stirring until present in slight excess as indicated by a faint odor of ammonia. If the precipitate does not have the characteristic reddish-brown color of ferric hydroxide, it shall be dissolved in hydrochloric acid, a few drops of ferric chloride solution shall be added, and the addition of a slight excess of ammonia shall be repeated. The solution shall be boiled for a few minutes, filtered, and the precipitate washed thoroughly with hot water.

4.2 The filtrate shall be evaporated to 175–200 ml., 1 ml. of 1 to 1 ammonium hydroxide and 3 g. of ammonium chloride added, and the solution heated to boiling. While the solution is being stirred, 10 ml. of saturated ammonium oxalate solution shall be added. The beaker shall be covered and set aside on a steam bath or warm place for not less than 2 hours nor more than 3 hours. The solution and precipitate shall be transferred quantitatively to a 250 ml. volumetric flask, cooled to 20° C., diluted to volume and mixed thoroughly. The solution shall be filtered through a dry, quantitative filter paper.

4.3 An aliquot of 100 ml., equivalent to 2 g. of the original leather, shall be transferred to a beaker, diluted to about 150 ml., made slightly acid to methyl orange with hydrochloric acid and cooled. Slightly more sodium ammonium hydrogen phosphate solution than is required to precipitate all of the magnesium shall be added (5 ml. is generally sufficient). While the solution is being vigorously stirred, ammonium hydroxide, 1:1, shall be added dropwise until the solution is faintly ammoniacal. After 15 minutes 5 ml. of concentrated ammonium hydroxide shall be added with stirring, the beaker shall be covered and left overnight at room temperature. Magnesium may then be determined by either the gravimetric or the volumetric procedure.

4.4 *Gravimetric procedure.* The solution shall be filtered through the crucible, and the precipitate washed on the crucible with 1 to 9 ammonium hydroxide until free from chlorides, moistened with 2 or 3 drops of ammonium nitrate solution and dried. The covered crucible and contents shall be ignited, gently at first, then at 1000–1100° C. for 1 hour or until its weight is constant.

4.5 *Volumetric procedure.* The solution shall be filtered through a close-textured filter paper. The precipitate, after transfer to the paper, shall be washed with a 1 to 9 ammonium hydroxide solution until free from chlorides. The ammonia shall be removed from the filter paper and the precipitate by one of the following methods:

4.5.1 The paper and precipitate shall be washed 3 or 4 times with neutral 60 per cent by volume methyl alcohol solution.

4.5.2 The paper shall be spread for a few minutes on coarse absorbent filter paper then on a watch glass for 1 hour at 50° C. (if 60° C. is exceeded the determination shall be discarded).

4.5.3 The paper shall be opened and allowed to dry overnight at room temperature.

4.6 The filter paper and ammonia-free precipitate shall be transferred to a beaker or flask, moistened with water and thoroughly disintegrated. A measured quantity of 0.1 *N* sulfuric acid, in excess of that required to react with the magnesium phosphate, 4 or 5 drops of the indicator, and sufficient water to make a volume of about 100 ml. shall be added. The excess acid shall be determined by titration with 0.1 *N* sodium hydroxide solution to the first appearance of green (the color change of the indicator is pink-grey-green).

5. RESULTS

5.1 The magnesium content (as Epsom salts) of the leather shall be calculated as follows:

5.1.1 For the gravimetric method (par. 4.4):

$$\text{Magnesium (as Epsom salts), per cent} = \frac{2.2147\ (W_2 - W_1)}{W_3} \times 100$$

where W_1 = the tare of the crucible,
W_2 = the weight of crucible and magnesium pyrophosphate ($Mg_2P_2O_7$)
W_3 = the weight of leather sample represented by the aliquot of the specimen (approximately 2 g.).

5.1.2 For the volumetric method (par. 4.5):

$$\text{Magnesium (as Epsom salts), per cent} = \frac{0.0123\ (V_1 - V_2)}{V_3} \times 100$$

where V_1 = the volume in ml. of sulfuric acid added,
V_2 = the volume of sodium hydroxide used to titrate the excess acid,
V_3 = the weight of leather represented by the aliquot.

ALCA Provisional Method May 1954.

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pH VALUE (B20)

1. SCOPE

1.1 This method is intended for use in determining the pH of a water extract of all types of vegetable-tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of from 2 to 5 g. of the sample prepared as directed in Method B1.

2.2 If the leather contains more than 8 per cent of petroleum ether extract on the dry basis, the weighed specimen shall be extracted with petroleum ether, boiling between 50° and 80° as directed in Method B3, then left at room temperature until all solvent has evaporated from it.

3. APPARATUS

3.1 A pH meter with glass electrode. The electrode should be calibrated with 0.05 molar potassium acid phthalate solution, pH 4.01, before making measurements.

4. PROCEDURE

4.1 The specimen shall be placed in a 250 ml. Pyrex flask, treated with 20 times the original specimen weight of freshly boiled, cooled, distilled water, the flask tightly stoppered and the mixture well agitated. After standing at room temperature for not less than 4 hours nor more than 18 hours,

the mixture shall be again well agitated, allowed to stand 10 minutes and the solution decanted. The pH of the decanted solution shall be measured with the glass electrode assembly.

5. RESULTS

5.1 The pH value shall be reported to the second decimal place.

ALCA Provisional Method May 1954

PROCTER AND SEARLE NUMBER (B21)

1. SCOPE

1.1 This method is intended for use in determining sulfuric acid in vegetable-tanned leather. It is not applicable to leathers that have been tanned with the addition of certain syntans.

2. SPECIMEN

2.1 The specimen shall consist of 2 g. of the sample prepared as directed in Method B1.

3. APPARATUS AND REAGENTS

3.1 An electric muffle furnace with temperature control.

3.2 A 100 ml. platinum dish.

3.3 Electric heater, Westinghouse 550W, 5 inch or similar.

3.4 Sodium carbonate solution, 0.1 normal.

3.5 Sulfuric acid solution, 0.1 normal.

4. PROCEDURE

4.1 The leather specimen shall be weighed into the platinum dish, treated with 40 ml. of the sodium carbonate solution, thoroughly mixed with the solution, then the solution shall be evaporated to complete dryness on a steam or water bath (the temperature during evaporation must not exceed 100° C.). The dish shall be placed in the cold muffle furnace and heated to 600°±10° C. in 2 hours, and maintained at that temperature for 1 hour. (The furnace should have vents either front or back, to permit access of air and removal of gases.)

4.2 The dish shall then be removed and cooled. The contents of the dish shall be carefully moistened with about 35 ml. of hot water and all lumps

broken up with a glass rod. The dish shall be covered and then heated by either (1) placing it on an electric heater with the bottom of the dish 0.75 inch above the element for 15 minutes, or (2) placing it on a steam bath so that a current of steam is in contact with the bottom of the dish for 30 minutes. (A water bath heated by gas or steam shall not be used.) The contents of the dish shall be filtered through an ashless filter paper into a 300 ml. flask, and the residue washed 4 or 5 times with hot water. The paper and residue shall be returned to the platinum dish and ignited at 600°±25° C. until all carbon has been burned. To the cool dish, a quantity of 0.1 *N* sulfuric acid shall be added that is exactly equivalent to the sodium carbonate solution (40 ml.) originally added to the leather. The dish shall be covered with a watch glass resting on a triangle supported by the dish, and heated on an electric heater for 15 minutes or a steam bath for 30 minutes exactly as described above. (High results will be obtained if the ash is not thoroughly digested with the acid.)

4.3 If the solution is clear, it shall be transferred quantitatively to the flask containing the filtrate. If the solution is sufficiently turbid to interfere with titration, it shall be filtered through a quantitative filter paper into the flask containing the first filtrate, and the paper shall be washed with hot water until free from acid. The solution shall be cooled and titrated to a clear yellow color with 2 or 3 drops of methyl orange and 0.1 *N* sodium hydroxide or 0.1 *N* sodium carbonate solution.

4.4 With each set of determinations a blank shall be run through the entire procedure. If the blank is more than 0.3 ml. the set of determinations must be repeated. The blank is not to be deducted from the results.

5. RESULTS

5.1 The percentage of sulfuric acid in the leather shall be calculated as follows:

$$\text{Sulfuric acid, per cent} = \frac{0.049 \times (V_1N_1 - V_2N_2)}{W} \times 100$$

where: N_1 = the normality of the standard alkali
N_2 = the normality of the standard acid
V_1 = the total volume of standard alkali used
V_2 = the volume of standard acid used
W = the weight of leather (2 grams)

5.1.1 In certain cases, especially of leathers treated with buffer salts to protect them from acid atmospheres, $(V_1N_1 - V_2N_2)$ may be negative. The result should be reported as such.

ALCA Provisional Method May 1954.

OFFICIAL CERTIFICATION (B30)

1. On public analytical work by members of this Association, the fact that the Official Method has been used shall be stated on the report.

2. The official form for the reporting of analyses of vegetable tanned leathers shall be as follows.

REPORT OF ANALYSIS

	Per Cent
Moisture	
Petroleum Ether Extract	
Insoluble Ash	
Hide Substance	
Soluble Nontannin	
Uncombined Tannin	
Combined Tannin	
Total	100.0%
Water Soluble Material	
Total Ash	
Magnesium, as Epsom Salts	
Glucose	
pH Value	
Degree of Tannage	

ALCA Provisional Method May 1954.

Method for the Analysis of Mineral Tanning Materials

CHROMIC OXIDE IN ONE BATH CHROME LIQUOR (C1)

1. SCOPE

1.1 This method is intended for use in determining the chromic oxide in one bath chrome liquors.

2. SPECIMEN

2.1 The specimen shall consist of a weighed quantity of the liquor diluted to a definite volume containing from 0.0015 to 0.0025 g. of Cr_2O_3 per ml.

3. APPARATUS AND REAGENTS

3.1 The apparatus and reagents shall be as described in Method D10, par. 3.1 (chromic oxide in chrome tanned leather, wet oxidation.)

4. PROCEDURE

4.1 The specimen shall be weighed to the nearest mg. before dilution. A 25 ml. aliquot of the diluted specimen shall be transferred to a small Erlenmeyer flask and treated as described in Method D10, per. 4.1.

5. RESULTS

5.1 The chromic oxide in the specimen shall be calculated as follows:

$$\text{Chromic oxide } (Cr_2O_3) \text{ per cent} = \frac{A \times N \times .02533}{W} \times \frac{V}{25} \times 100$$

where:

A = the number of ml. of standard thiosulfate (or ferrous sulfate) required to titrate the 25 ml. aliquot of the specimen.
N = the normality of the thiosulfate (or ferrous sulfate) solution.
W = the weight of the specimen before dilution, grams.
V = the volume to which W was diluted, ml.

5.2 Unless otherwise specified in the detail specifications, two 25 ml. aliquots from the diluted specimen shall be tested.

5.3 The chromic oxide in the sample for test shall be the average of the test results obtained from the two aliquots tested.

5.4 The chromic oxide in the sample shall be recorded to the nearest 0.1 per cent.

ALCA Provisional Method May 1954.

ACID IN ONE BATH CHROME LIQUOR (C5)

1. SCOPE

1.1 This method is intended for use in determining the acid in one bath chrome liquors.

2. SPECIMEN

2.1 The specimen shall be as described in Method C1.

3. APPARATUS AND REAGENTS

3.1 A 7 inch casserole.

3.2 Sodium hydroxide, 0.1 *N* solution, standardized.

3.3 Phenolphthalein, 5% in 95% ethyl alcohol.

4. PROCEDURE

4.1 The specimen shall be weighed to the nearest mg. before dilution. A 25 ml. aliquot of the diluted specimen shall be transferred to the casserole. 400 ml. of water and 1 ml. of 5% phenolphthalein shall be added and the contents brought to a boil. While boiling it shall be titrated with 0.1 *N* sodium hydroxide until the pink color, seen at the side of the casserole after the precipitate has settled, persists for 1 min.

5. RESULTS

5.1 The acid in the specimen shall be calculated as follows:

$$\text{Sulfuric acid } (H_2SO_4) \text{ per cent} = \frac{A \times N \times .049}{W} \times \frac{V}{25} \times 100$$

where:

A = the number of ml. of standard sodium hydroxide required to titrate the 25 ml. aliquot of the specimen.

N = the normality of the sodium hydroxide.

W = the weight of the specimen before dilution, grams.

V = the volume to which the specimen was diluted, ml.

5.1.1 If the acid is hydrochloric acid replace .049 by .0365 in par. 5.1.

5.2 Unless otherwise specified in the detail specification, two 25 ml. aliquots of the specimen shall be tested.

5.3 The acid in the sample for test shall be the average of the test results obtained from the two aliquots tested.

5.4 The acid in the sample shall be recorded to the nearest 0.1 per cent.

ALCA Provisional Method May 1954.

BASICITY IN ONE BATH CHROME LIQUOR (C10)

1. SCOPE

1.1 This method is intended for use in calculating the basicity of one bath chrome liquors.

2. SPECIMEN

2.1 The specimen shall be as described in Method C1.

3. APPARATUS AND REAGENTS

3.1 The apparatus and reagents shall be as described in Methods C1 and C5, par. 3.

4. PROCEDURE

4.1 The chromic oxide shall be determined as described in Method C1, par. 4. The acid shall be determined as described in Method C5, par. 4.

5. RESULTS

5.1 The basicity of the specimen shall be expressed according to Schorlemmer's system. In this system, the basicity is the per cent of the total chromic oxide that is combined with hydroxyl and is calculated as follows.

Basicity, per cent =

$$100 - \frac{\%\ H_2SO_4}{\%\ Cr_2O_3} \times 51.5 \text{ for a sulfate liquor}$$

$$100 - \frac{\%\ HCL}{\%\ Cr_2O_3} \times 69.45 \text{ for a chloride liquor}$$

$$\frac{A - B}{A} \times 100 \qquad \text{for either liquor}$$

where:

A = the amount of sodium thiosulfate, as ml. of *N* solution, required to titrate the 25 ml. aliquot of the specimen in Method C1.

B = the amount of sodium hydroxide, as ml. of *N* solution to titrate the 25 ml. aliquot of the same specimen in Method C5.

5.2 Unless otherwise specified in the detail specification, two specimens from the composite sample shall be tested.

5.3 The basicity of the sample for test shall be the average of test results obtained from the specimens tested.

5.4 The basicity of the sample shall be recorded to the nearest 0.1 per cent.

ALCA Provisional Method May 1954.

SAMPLING OF MINERAL TANNED LEATHER FOR CHEMICAL TESTS (J25)

1. SCOPE

1.1 This procedure is intended for use in sampling all types of mineral

tanned leather. The sample obtained shall be used for preparing a composite sample for chemical tests. (See Method D1.)

2. DEFINITIONS OF HIDE PARTS

2.1 The definition of hide parts shall be as described in J2.

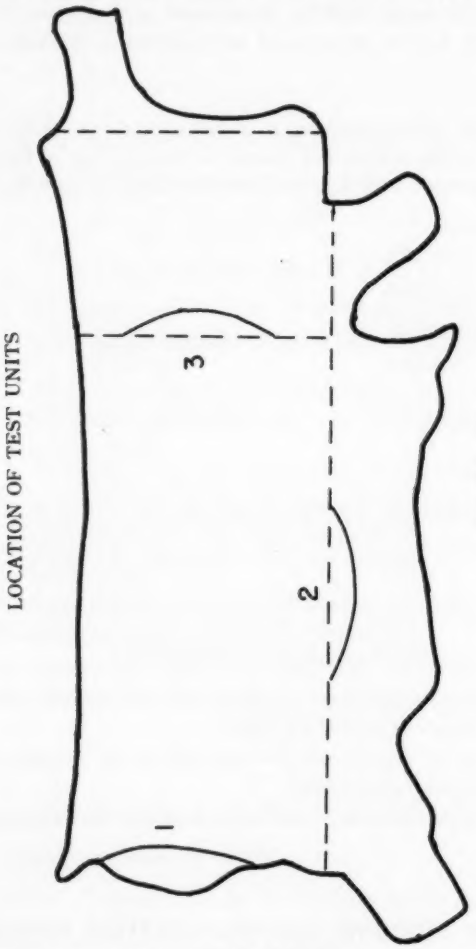

FIGURE J25

3. NUMBER OF UNITS TO BE SAMPLED

3.1 Fifteen units shall be selected at random for test from each lot. For lots consisting of less than fifteen units, each unit shall be sampled for test.

4. LOCATION AND SIZE OF TEST UNITS

4.1 All test units shall be cut to give a piece approximately 8 inches long by 3 inches wide.

4.2 The locations from which test units are to be cut are indicated in Figure J25.

4.2.1 For all units except bellies and double shoulders, the test units shall be cut from position 1.

4.2.2 For bellies, the test units shall be cut from position 2.

4.2.3 For double shoulders, the test units shall be cut from position 3.

ALCA Provisional Method May 1954.

Methods for the Analysis of Mineral Tanned Leathers

PREPARATION OF COMPOSITE SAMPLE FOR CHEMICAL TESTS (D1)

1. SCOPE

1.1 This method is intended for use in preparing a representative composite sample of leather in a form suitable for chemical analysis.

2. COMPOSITE SAMPLE

2.1 The composite sample shall consist of equal portions from each test unit of the sample taken for test according to Method J25. Alternatively, the scraps from the sample taken for physical tests according to Methods J1 or J2 may be used.

3. APPARATUS

3.1 Scissors, knife or other tool suitable for cutting leather.

3.2 Balance that will weigh to an accuracy of 1 g.

3.3 Wiley mill with 4 mm. sieve for grinding leather.

3.4 Stoppered bottle or other container for storing the composite sample.

4. PROCEDURE

4.1 After removing a strip about ½ inch wide from the uncut edge, each portion from each test unit shall be weighed on a balance and adjusted to within 1 g. of the same weight. All portions taken shall be cut into pieces approximately ½ inch square, mixed well and ground in a Wiley mill until all the material has passed through the 4 mm. sieve. The ground material shall be mixed well and stored in a tightly stoppered container. Specimens for tests in Method D5 shall be taken from this composite sample.

ALCA Provisional Method May 1954.

MINERAL LEATHERS – GENERAL (D5)

1. SCOPE

1.1 These methods are intended for use in the chemical analysis of mineral tanned leathers.

2. SAMPLES AND SPECIMENS

2.1 The samples shall be taken in accordance with Method J25 and the preparation of the composite sample of mineral tanned leather, from which specimens are to be taken for analysis, shall be as described in Method D1.

3. APPARATUS AND REAGENTS

3.1 All volumetric glassware used in the chemical analysis shall comply with the specifications for Class B of Federal Specification DD-V-581, Volumetric Apparatus, Glass.

3.2 Unless otherwise specified, all reagents used in the chemical analysis shall comply with specifications recommended by the Committee on Analytical Reagents of the American Chemical Society.

3.3 The distilled water used in the chemical analysis shall have a pH of not less than 5.5 nor more than 7.0 and shall give a residue of not more than 0.0005 g. when 100 ml. is evaporated and dried in a platinum dish.

3.4 General laboratory apparatus and reagents shall be available. (Special apparatus and reagents are described in the individual methods.)

4. PROCEDURE

4.1 *Moisture.* Moisture shall be determined as in Method B2.

4.2 *Organic Solvent Extract.* The organic solvent extract shall be determined as in Method B4, employing chloroform as the solvent. The materials extracted by this test are normally considered as the fat or grease content of the leather.

4.3 *Total Nitrogen.* The nitrogen content of the mineral tanned leather shall be determined as described in Method B5, using 1.4 g. (or 0.5 g.) sample for analysis. The percentage of nitrogen multiplied by 5.62 shall give the percentage of hide substance.

4.4 *Total Ash.* Total ash shall be determined as outlined in Method B15, except that the specimen taken for analysis shall consist of 0.5 to 2.0 g. accurately weighed.

4.5 *Chromic Oxide.* Chromic oxide shall be determined as in Method D10.

4.6 *Sulfates.* The total, neutral and combined acid sulfates shall be determined as in Method D20.

4.7 *Chlorides.* The total chlorides shall be determined as described in Method D21.

4.8 *Sulfate Basicity.* The sulfate basicity shall be calculated as outlined in Method D30.

4.9 *Acidity (pH Value).* The pH value of the mineral tanned leather shall be determined as in Method D35.

ALCA Provisional Method May 1954.

CHROMIC OXIDE IN LEATHER (D10)

1. SCOPE

1.1 This method is intended for use in determining the chromic oxide content of leather. Alternative procedures are provided for oxidizing the specimen and for titrating the dichromate produced by the oxidation.

2. SPECIMEN

2.1 For the *wet oxidation* procedure, the specimen shall consist of sufficient leather from the composite sample (Method D1) to contain from 0.05 to 0.10 g. of chromic oxide.

2.2 For the *alkaline fusion oxidation* procedure the specimen shall consist of sufficient leather from the composite sample (Method D1) to contain from 0.1 to 0.25 g. of chromic oxide.

3. APPARATUS AND REAGENTS

3.1 The apparatus and reagents for *wet oxidation* shall be as follows:

3.1.1 Perchloric acid, 72%, reagent grade.

3.1.2 Sulfuric acid, reagent grade.

3.1.3 Nitric acid, reagent grade.

3.2 The apparatus and reagents for *oxidation by alkaline fusion* shall be as follows:

3.2.1 Platinum crucible.

3.2.2 Fused powdered borax, reagent grade.

3.2.3 Potassium carbonate, reagent grade.

3.2.4 Sodium carbonate, reagent grade.

3.3 The apparatus and reagents for the *titration by thiosulfate* shall be as follows:

3.3.1 Phosphoric acid, 40% solution.

3.3.2 Sodium thiosulfate, 0.1 *N* standardized.

3.3.3 Starch indicator, 2% solution.

3.3.4 Potassium Iodide, 10% solution, reagent grade (Iodate free).

3.4 The apparatus and reagents for the *titration by ferrous sulfate* shall be as follows.

3.4.1 Ferrous sulfate solution, 0.1 *N* standardized.

3.4.2 Electrometric titrimeter or oxidation-reduction indicator.

4. PROCEDURE

4.1 *Wet Oxidation.* The specimen shall be weighed to the nearest mg. and the value recorded as *W*. The specimen (or the ash from Method D1, Total Ash) shall be transferred to a 250 ml. Erlenmeyer flask and treated with 20 ml. of conc. nitric acid, 15 ml. of 70% perchloric acid, and 10 ml. of conc. sulfuric acid. The mixture shall be heated under reflux conditions, using a small funnel for a condenser, until the color changes to reddish-orange and for an additional 2 minutes to insure complete oxidation. The solution shall be cooled and diluted to approximately 125 ml. with distilled water. The solution shall be boiled (anti-bump chips or beads may be added) to drive off excess chlorine. (A negative test, when potassium iodide paper is held in the vapors, indicates that the chlorine has been driven off.) The solution shall be cooled and titrated by the procedure described in either par. 4.3 or 4.4

4.1.1 At this point in the analysis, the oxides of aluminum, iron, zirconium and titanium may be determined, if desired, by conventional methods.

4.2 *Alkaline fusion method.* The specimen shall be weighed to the nearest mg. and the value recorded as *W*. The specimen shall be transferred to a platinum crucible and ashed according to Method D5.

4.2.1 Six g. of a fusion mixture consisting of 2 g. of sodium carbonate, 2 g. of potassium carbonate, and 2 g. of fused powdered borax shall be well mixed with the ash in the crucible and the mixture fused for 30 minutes over an oxidizing flame. The fused mass shall be cooled, transferred to a 400 ml. beaker and dissolved in hot distilled water. The solution shall be filtered into another 400 ml. beaker and the paper and residue washed with hot distilled water, adding the washings to the filtrate. If required, an analysis for the oxides of iron, zirconium, and titanium may be performed on the residue in the filter paper at this point. If aluminum oxide is to be determined, the analysis may be performed on an aliquot of the solution in par. 4.2.2.

4.2.2 The solution shall be boiled for a few minutes, filtered into a 500 ml. volumetric flask and the residue washed with hot distilled water, adding the washings to the filtrate. After cooling, the solution shall be made up to the mark with distilled water and well mixed. Of this solution, 200 ml. shall be pipetted into a 500 ml. Erlenmeyer flask, 10 ml. of conc. hydrochloric acid added and the solution titrated by either procedure described in par. 4.3 or 4.4.

4.3 *Titration with sodium thiosulfate.* Thirty ml. of 40% phosphoric acid (to complex iron) and 10 ml. of potassium iodide shall be added to the solution, mixed and the solution allowed to stand 2 minutes with the flask stoppered. The solution shall be titrated immedately with 0.1 *N* sodium

thiosulfate solution using starch indicator near the end of the titration.

4.4 *Titration with ferrous sulfate.* After adding 1 ml. of 85% phosphoric acid the solution shall be titrated with 0.1 *N* ferrous sulfate using either an electrometric titrimeter or an oxidation-reduction indicator to indicate the end point.

5. RESULTS

5.1 The chromic oxide in the specimen from the *wet oxidation* procedure shall be calculated as folows:

$$\text{Chromic Oxide } (Cr_2O_3) \text{ per cent} = \frac{A \times N \times 0.02533 \times 100}{W}$$

where: A = the ml. of titrating reagent used
N = the normality of the titrating reagent
W = the weight of the specimen in grams

5.2 The chromic oxide in the specimen from the *alkaline-fusion* procedure shall be calculated as follows:

$$\text{Chromic Oxide } (Cr_2O_3) \text{ per cent} = \frac{A \times N \times 0.02533 \times 2.5 \times 100}{W}$$

where: A = the ml. of titrating reagent used
N = the normality of the titrating reagent
W = the weight of the specimen in grams

5.3 The chromic oxide on the hide substance basis shall be calculated as follows.

$$\text{Chromic oxide } (Cr_2O_3) \text{ on hide substance, per cent} = \frac{B}{C} \times 100$$

where: B = the per cent chromic oxide on moisture free basis
C = the per cent hide substance on a moisture free basis

5.4 Unless otherwise specified in the detail specification, 2 specimens from the composite sample shall be tested.

5.4.1 The chromic oxide in the sample shall be reported as the average of the test results from the specimens tested.

5.4.2 The chromic oxide in the sample shall be reported to the nearest 0.1% on the moisture free, or the moisture and grease free basis, or the hide substance basis.

ALCA Provisional Method May 1954.

SULFATES (TOTAL, NEUTRAL AND COMBINED ACID) (D20)

1. SCOPE

1.1 These methods are intended for use in determining the total, neutral, and combined acid sulfate in mineral-tanned leather.

2. SPECIMEN

2.1 The specimen for each determination shall consist of 1 g. leather, from the composite sample, Method D1.

3. APPARATUS AND REAGENTS

3.1 Volumetric flask, 250 ml.

3.2 Ashless fine grained filter paper and porcelain crucible. Optional: Gooch crucible with asbestos pad or porous porcelain filter crucible.

3.3 Ammonium hydroxide, 0.1 *N* solution (7 ml. per liter reagent grade conc. NH_4OH). Optional: Potassium dihydrogen phosphate, 0. 1 molar solution (13.6 g/1 KH_2PO_4) or sodium dihydrogen phosphate, 0.1 molar solution (13.8 g/1 NaH_2PO_4–H_2O).

3.4 Hydrochloric acid, 1.5 *N* solution (125 ml. per liter reagent grade conc. hydrochloric acid).

3.5 Barium chloride ($BaCl_2 \cdot 2H_2O$), 1 per cent solution.

3.6 Sodium hydroxide, 0.01 *N* solution (0.4 g/1).

3.7 Mixed Indicator, consisting of 60 ml. of a 0.1 per cent solution of methyl red and 40 ml. of a 0.1 per cent solution of methylene blue, both in 95 per cent alcohol.

4. PROCEDURE

4.1 *Total Sulfates.* The specimen shall be weighed to the nearest mg. and the value recorded as W_1. The specimen shall be transferred to a 250 ml. volumetric flask to which 200 ml. of 0.1 *N* ammonium hydroxide or 0.1 molar potassium or sodium dihydrogen phosphate solution shall be added. The flask shall be immersed up to the neck in a bath of boiling water. All particles shall be thoroughly wetted by swirling occasionally. After 2 hours the flask shall be cooled to room temperature, made up to volume with distilled water, shaken and without delay filtered through a folded filter paper. The first 20 to 25 ml. of the filtrate shall be discarded. 200 ml. of the filtrate shall be pipetted into a 600 ml. beaker and about 20 ml. 1.5 *N* hydrochloric acid shall be added. The solution shall be heated to boiling and while boiling and stirring the solution, 20 ml. of a one per cent solution of barium chloride shall be added dropwise. The covered beaker shall be kept in a warm place at least for two hours and preferably over night.

4.1.1 The precipitate shall be filtered through a fine grained ashless filter paper and washed with hot water until free from chloride. Alternatively a weighed Gooch crucible with asbestos pad or a weighed porous crucible may be used for the filtration. The paper with the precipitate shall be transferred to a weighed crucible and ignited gently, either over a gas burner or in a muffle oven at 900° C. for one hour. The crucible shall be cooled in a desiccator, weighed and the value of the $BaSO_4$ recorded as W_2.

4.2 *Neutral Sulfates.* The specimen shall be weighed to the nearest mg. and the value recorded as W_3. The specimen shall be transferred to a 250 ml. volumetric flask to which 200 ml. of distilled water shall be added. The flask shall be immersed up to the neck in boiling water. All particles shall be throughly wetted by swirling occasionally. After 2 hours the flask shall be cooled to room temperature, made up to volume with distilled water, shaken and without delay filtered through a folded filter. The first 20 to 25 ml. of the filtrate shall be discarded. 200 ml. of the filtrate shall be pipetted into a 600 ml. beaker and titrated with 0.01 *N* sodium hydroxide, using a few drops of the mythyl red/methylene blue indicator. The results shall be recorded as ml. 0.01 *N* NaOH. After addition of 4 to 5 ml. 1.5 *N* hydrochloric acid the solution shall be heated to boiling and while boiling and stirring the solution, 10 ml. of a one per cent barium chloride solution shall be added dropwise. The covered beaker shall be kept in a warm place at least for two hours and preferably over night.

4.2.1 The directions of 4.1.1 shall be adhered to. The value of the $BaSO_4$ shall be recorded as W_4.

5. RESULTS

5.1 The total sulfate content of the specimen shall be calculated as follows:

$$\% \text{ Total sulfate } (SO_4) = \frac{W_2 \times .4115}{W_1} \times \frac{250}{200} \times 100$$

where: W_1 = the weight of the specimen
W_2 = the weight of the $BaSO_4$

5.2 The neutral sulfate content of the specimen shall be calculated as follows.

$$\% \text{ Neutral sulfate } (SO_4) = \frac{(W_4 \times .4115 - N \times A \times .048)}{W_3} \times \frac{250}{200} \times 100$$

where: W_3 = the weight of the specimen
W_4 = the weight of the $BaSO_4$
A = the ml. of standard NaOH
N = the normality of the standard NaOH

5.3 The combined acid sulfate content of the specimen shall be calculated as follows:

Combined acid sulfate (SO_4) per cent = % total sulfate − % neutral sulfate.

5.4 Unless otherwise specified in the detail specification, two specimens from the composite sample shall be tested for each determination.

5.4.1 The total, neutral and combined acid sulfates in the sample for test shall be the average of the test results obtained from the specimens tested.

5.4.2 The results shall be reported to the nearest 0.1 per cent.

ALCA Provisional Method May 1954.

TOTAL CHLORIDES (D21)

1. SCOPE

1.1 This method is intended for use in determining total chlorides in mineral tanned leather.

2. SPECIMEN

2.1 The specimen shall consist of 1 g. of leather from the composite sample, Method D1.

3. APPARATUS AND REAGENTS

3.1 Volumetric flask, 250 ml.

3.2 Acetic acid solution, 5 or 10 per cent by volume.

3.3 Methyl Orange, 0.02 per cent solution in 50 per cent alcohol.

3.4 Ammonium hydroxide 0.1 *N* solution.

3.5 Silver nitrate, 0.1 *N* solution, standardized.

3.6 Potassium chromate, 5 per cent solution.

4. PROCEDURE

4..1 The specimen shall be weighed to the nearest mg. and the value recorded as W. The specimen shall be transferred to a 250 ml. volumetric flask to which 200 ml. of 0.1 *N* ammonium hydroxide solution shall be added. The flask shall be immersed up to the neck in a bath of boiling water. All particles shall be thoroughly wetted by occasional swirling. After 2 hours the flask shall be cooled to room temperature, made up to volume with distilled water, shaken and without delay filtered through a folded filter paper.

4.2 The first 20 to 25 ml. of the filtrate shall be discarded. 200 ml. of the filtrate shall be pipetted into a 600 ml. beaker, a few drops of methyl orange

indicator added and neutralized with 5 per cent acetic acid to an orange color. 2 to 3 ml. of 5 per cent potassium chromate shall be added and the solution titrated with 0.1 *N* silver nitrate. The ml. of silver nitrate used shall be recorded as A. 200 ml. of distilled water containing a few drops of methyl orange indicator and 2 to 3 ml. of 5 per cent potassium chromate shall be titrated with 0.1 *N* silver nitrate as a blank and the ml. of silver nitrate used recorded as B.

5. RESULTS

5.1 The per cent total chlorides shall be calculated as follows.

$$\text{Total chlorides, per cent} = \frac{(A-B)\,N}{W} \times .0355 \times \frac{250}{200} \times 100$$

where: A = the ml. of standard silver nitrate used for titrating the sample.
B = the ml. of standard silver nitrate used for titrating the blank
N = the normality of the standard silver nitrate
W = the weight of the specimen

5.2 Unless otherwise specified in the detail specification, two specimens from the composite sample shall be tested.

5.2.1 The total chlorides in the sample for test shall be the average of the test result obtained from the specimens tested.

5.2.2 The result shall be reported to the nearest 0.1 per cent.

ALCA Provisional Method May 1954.

SULFATE BASICITY (D30)

1. SCOPE

1.1 This method is intended for use in calculating the sulfate basicity of mineral tanned leather.

2. SPECIMEN

2.1 The specimen shall be as described in Methods D10 and D20 (chromic oxide and sulfates in leather).

3. APPARATUS AND REAGENTS

3.1 The apparatus and reagents shall be as described in Methods D10 and D20 (chromic oxide and sulfates in leather).

4. PROCEDURE

4.1 The chromic oxide shall be determined as described in Method D10 (chromic oxide in leather). The combined sulfate shall be determined as described in Method D20 (sulfates in leather).

5. RESULTS

5.1 The per cent basicity of the specimen shall be expressed according to Schorlemmer's system. In this sytem, the per cent basicity is the per cent of the total chromic oxide that is combined with hydroxyl. Conversely, the per cent acidity is the per cent of the total chromic oxide that is combined with sulfate or other acid anions. Per cent basicity is therefore 100 – per cent acidity.

$$\text{Sulfate basicity, per cent} = 100 - \frac{\%\ \text{combined sulfate} \times 52.8}{\%\ \text{total chromic oxide}}$$

5.1.2 When other metals that form hydrolysable sulfates are present, their equivalent per cent of chromic oxide shall be added to the chromic oxide present before calculating per cent basicity. The following conversion factors shall be used:

$$\%\ Al_2O_3 \times 1.49$$
$$\%\ ZrO_3 \times 0.82$$
$$\%\ Fe_2O_3 \times 0.95$$

5.2 Unless otherwise specified in the detail specifications two specimens from the composite sample shall be tested.

5.2.1 The per cent basicity of the sample for test shall be the average of the test results obtained from the specimens tested.

5.2.2 The result shall be reported to the nearest 0.1 per cent.

ALCA Provisional Method May 1954.

ACIDITY (pH) (D35)

1. SCOPE

1.1 This method is intended for use in determining the pH of a cold water extract of mineral-tanned leather and is held to be a measure of the acidity of the leather.

2. SPECIMEN

2.1 The specimen shall consist of 3 g. of leather, from the composite sample, Method D1.

3. APPARATUS

3.1 The apparatus shall consist of a pH meter with glass electrodes.

4. PROCEDURE

4.1 The specimen shall be weighed to the nearest 0.01 g. If the specimen contains 10 per cent or more of grease it shall be solvent extracted as described in Method D5 and the residue dried at room temperature.

4.2 The specimen shall be transferred to a 250 ml. flask and 20 times its weight of freshly boiled and cooled distilled water added. The flask shall be tightly stoppered, the mixture agitated throughly and set aside with occasional agitation for a period of 4 to 18 hours. The mixture shall again be throughly agitated, set aside for the residue to settle and the liquid decanted into a beaker. The pH of the decanted liquid shall be determined with the pH meter at room temperature.

5. RESULTS

5.1 The pH of the sample shall be recorded to nearest 0.1 unit.

5.2 The pH of the sample for test shall be the average of the test results obtained from the specimen tested.

5.3 Unless otherwise specified in the detail specification, two specimens from the composite sample shall be tested.

ALCA Provisional Method May 1954.

The Absorption of Ligninsulphonates by Hide Powder*

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During recent years, interest in the use of waste lignin products, particularly sulphite waste liquor, as a tanning agent has greatly increased. This interest has grown partly through the increased shortage of natural tanning materials and partly through the increased efforts which have been made to find a satisfactory use for this cheap and plentiful by-product. Experimental and industrial experience has shown that sulphite waste liquor is not a satisfactory tanning agent but that it may be used successfully as an extender for the natural tanning materials.

Although a large number of investigations have been carried out on the utilization of sulphite waste liquor as a tanning agent, there is still a lack of

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fundamental knowledge of the reaction between ligninsulphonic acid and collagen, the protein present in hide substance. Much of this earlier work suffers from the fact that it has been carried out on the crude sulphite waste liquor, about half of which is composed of sugars and inorganic materials, the remainder being ligninsulphonic acids of widely different molecular weights. Furthermore, sulphite waste liquors vary appreciably according to the cooking conditions, species of wood, etc., and experiments based on liquors of different origin are therefore subject to considerable error. No standard method is available for evaluating the tannin content of lignin extracts similar to the Official Method which has been adopted for the vegetable tannins[1]. This method has been found to be unsatisfactory when applied to lignin containing materials[2, 3, 4, 5].

The present investigation has been concerned with the elucidation of some of the factors involved in the reaction between carefully purified ligninsulphonic acids and hide powder with a view to providing a satisfactory method for measuring the amount of lignin absorbed by hide powder, and further to provide some information on the relative absorption properties of ligninsulphonic acid fractions and their salts.

Experimental

Preparation and Analysis of Ligninsulphonic Acids

The raw material was a commercially fermented sulphite waste liquor, supplied by a mill producing a newsprint grade of sulphite pulp by using a liquor with a high SO_2 content on a mixture of spruce and balsam (See

TABLE 1

Analysis of Fermented Sulphite Waste Liquor*

Total Solids	87.0 g. per litre
Methoxyl Content of Total Solids	7.5 %
Ligninsulphonic Acid Content (based on a methoxyl content of 12.3%)	61.0 %
Calcium Content of Total Solids (as CaO)	8.0 %
Ash Content of Total Solids	13.0 %

*The fermented sulphite waste liquor was kindly provided by the Ontario Paper Company, Thorold, Ontario.

Table I). It was placed in cellophane membranes and dialyzed in a large bath of de-ionized water until substantially free of sugars. This required approximately 10 days, the water in the bath being changed after the third and seventh day. The dialysate was also recovered and evaporated under reduced pressure for subsequent recovery of the sugars and low molecular ligninsulphonic acids. The solids and methoxyl recovery on dialysis are shown in Table II.

TABLE II

Recovery of Solids and Methoxyl on Dialysis

	Fermented SWL	Dialysate	Dialyzed Material
Volume (ml.)	1,000	19,160	1,770
Total Solids (g.)	87.0	47.7	36.8
Methoxyl Content of Total Solids (%)	7.5	4.8	11.6
Methoxyl Content of Total Solids (g.)	6.5	2.2	4.2

The dialyzed material, after decalcification by passing through a column containing Amberlite IR-100, had a negligible ash content and was considered to be pure high molecular ligninsulphonic acids (see Table III).

TABLE III

Analysis of Ligninsulphonic Acid Fractions

	Non Tannin Portion of Low Molecular Ligninsulphonic Acids	Low Molecular Ligninsulphonic Acid	High Molecular Ligninsulphonic Acid
1. Free SO_2	nil	nil	nil
2. Loosely Combined SO_2		0.47%	0.59%
3. Total Sulphur	2.3%	6.5%	6.1%
4. Methoxyl Content	4.8%	9.7%	12.3%
5. Titration (milliequivalents NaOH per gram to pH 7	0.79	2.25	1.98
6. Reducing Sugar Content	nil	nil	nil

The dialysate was de-ashed by adsorption on columns containing Amberlite IR-100 and IR-4B, respectively, then neutralized to a pH of 6.5 with ammonia, and the sugars removed by adsorption on Amberlite IR-A400 according to the method of Yorston[6]. The resulting low molecular ligninsulphonic acid fraction still gave a slight test with Fehling solution but showed the complete absence of sugars when analyzed by paper strip chromatography (see Table III).

Effect of pH on the Absorption of Calcium, Magnesium, Sodium and Ammonium Ligninsulphonates

A comparison was made of the relative asborption of the Ca, Mg, Na and NH_4 ligninsulphonates over a wide range of pH. In order to make this comparison as exact as possible these salts were prepared by neutralizing portions of the same purified high molecular ligninsulphonic acid (Table III) with CaO, $MgCO_3$, NaOH and $(NH_4)_2CO_3$ respectively. The titration curves are shown in Figure I. Samples were removed at various pH levels and after adjustment to a concentration of 1% total solids the absorption was measured by the standard Hide Powder Method of the American Leather Chemists

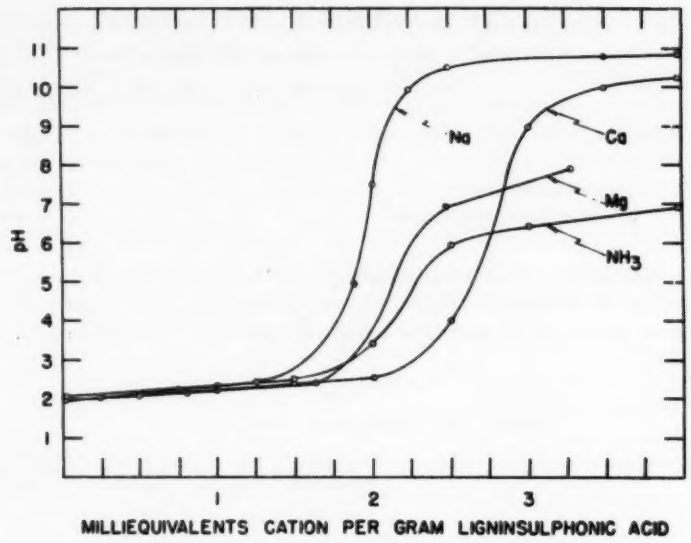

FIGURE I.—Potentiometric Titration of High Molecular Ligninsulphonic Acid with Various Alkalis

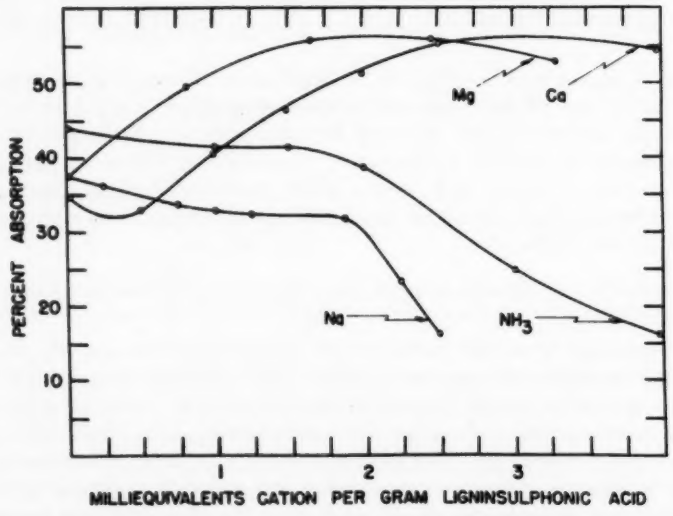

FIGURE II.—Effect of pH on Absorption of High Molecular Ligninsulphonates.

Association. The results, shown in Figure II, indicate that the absorption of the high molecular ligninsulphonates is dependent, not only on pH, but on the base used for adjusting the pH. In the case of the divalent salts Ca and Mg, absorption increased up to a pH of 3 and then remained essentially constant. The absorption of the monovalent salts sodium and ammonium decreased with increasing pH, this decrease becoming very marked above a pH of 3. Contrary to prevailing opinion, the divalent salts appear to have a more favourable absorption than the monovalent salts.

Effect of Temperature

Salvesen [5] has carried out a systematic investigation of the effect of temperature on the absorption of ligninsulphonates by hide powder. He reported that 98 to 100% of the ligninsulphonate present in sulphite waste liquors is absorbed by the hide powder within the official 10 minute shaking time, if the temperature of the solution is raised to 45°. Thus by increasing the temperature from 23° to 45°, the purity of commercial lignin extracts, as determined by the official procedure, increased from 50–55% to 70% or higher. Since Salvesen did not present any experimental data it was considered worthwhile to include the results obtained in the present investigation on the effect

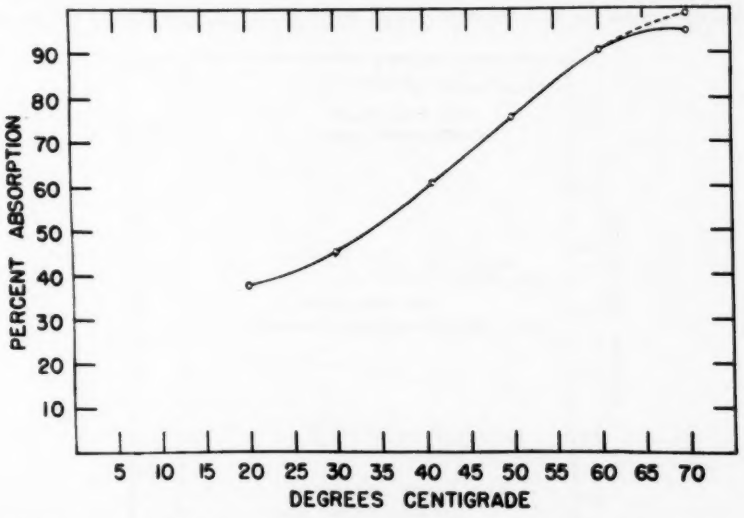

FIGURE III.—Effect of Temperature on Absorption of High Molecular Ligninsulphonic Acid.

(The solid line shows the results actually obtained. The broken line shows the results obtained after deducting the amount of hide powder dissolved in an equal volume of water under identical conditions).

of temperature as one of the important variables in the absorption of ligninsulphonates by hide powder. The Official Hide Powder Method was used with the exception of a slight change in the shaking procedure. In order to carry out this operation at different temperatures it was found more convenient to stir the hide powder in the lignin solution with a mechanical stirrer in a 500 ml. round bottom flask fitted with a thermometer and a reflux condenser. The apparatus was placed in a constant temperature bath and the hide powder added after the lignin solution had reached the desired temperature.

The results obtained, using a purified high molecular ligninsulphonic acid (pH = 2.0), are shown in Figure III. The rate of absorption was found to increase rapidly with increasing temperature, essentially complete absorption being obtained in 10 minutes at 70°. This temperature is somewhat higher than that reported by Salvesen for complete absorption and is probably due to the much lower rate of absorption of the free ligninsulphonic acid as compared with its salts.

Effect of Time on the Absorption of Ligninsulphonic Acids by Hide Powder

The effect of time on the absorption of various ligninsulphonates was also studied using the Official Hide Powder Method and extending the 10 minute shaking period for various intervals up to 80 minutes. The results are shown

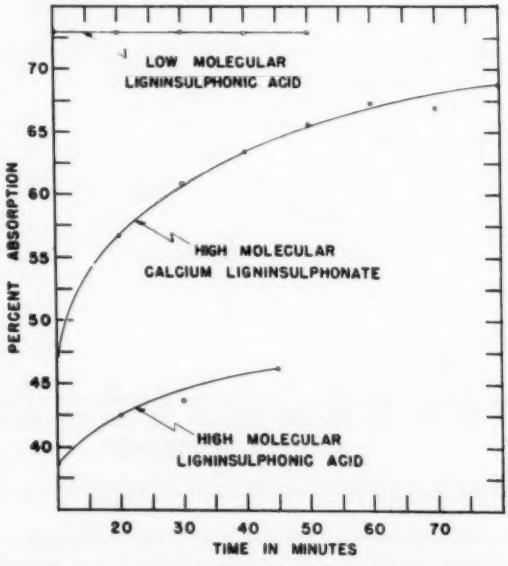

FIGURE IV.—Effect of Time on Absorption of Various Ligninsulphonates by Hide Powder.

in Figure IV. In the case of the high molecular fraction, both the Ca salt and the free acid were found to be absorbed very slowly as compared with the natural tannins in which the absorption is complete in the 10 minute shaking period. This again confirms Salvesen's conclusion that the Hide Powder Method gives low inaccurate results when applied to lignin compounds.

The low molecular ligninsulphonic acid fraction gave quite different results. The rate of absorption was much more rapid and levelled off to a constant value of 72.3% during the first 10 minutes of contact with the hide powder. This value appeared to be a maximum since it could not be increased by prolonging the time or raising the temperature. These results suggested that the low molecular fraction did not consist wholly of lignin compounds in spite of the fact that it has been carefully de-ashed and freed of sugars by ion exchange treatment. The remaining 27.7% therefore appears to be one or more components not previously identified in sulphite waste liquor. The isolation and analysis of this material is discussed in a later section of this Report.

Effect of Concentration on the Absorption of Ligninsulphonic Acids by Hide Powder

A study of the effect of concentration was also carried out by the Official Procedure using a constant volume of 200 ml. of lignin solution and varying

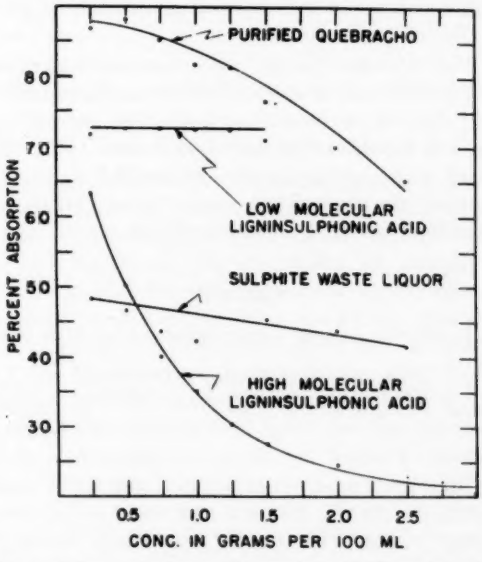

FIGURE V.—Effect of Concentration on Absorption of Ligninsulphonic Acids and Quebracho by Hide Powder.

the concentration. A commercial quebracho extract, purified by dialysis in de-ionized water for 10 days, was included for comparison. The results are shown in Figure V. The low molecular ligninsulphonic acids showed no change in absorption at concentrations of 0.25 – 1.50% indicating that absorption was complete under these conditions. The high molecular fraction however was only partially absorbed and thus showed a marked change in absorption value with increasing concentration. This change was not nearly so marked in the case of sulphite waste liquor probably because it contains a high percentage of non-reactive materials and also low molecular weight ligninsulphonic acids which are rapidly absorbed. The slight change in absorption value obtained with quebracho indicates that it is not completely absorbed under these conditions and that its rate of absorption lies between that of the low and high molecular weight ligninsulphonic acids.

The Equilibrium Between Ligninsulphonates and Hide Powder

The equilibrium between hide powder and various ligninsulphonates in aqueous solution was also studied. Gustavson has stated that ligninsulphonic acids are absorbed irreversibly by hide substance and thus fulfill the first fundamental requirement of a tanning agent[7]. This property is of considerable importance, not only in tanning, but in its application to lignin chemistry. It was therefore considered worthwhile to extend this study to the purified ligninsulphonates and to other components of the sulphite waste liquor.

The Official Hide Powder Test for tannin content was carried out on five materials, using in each case a series of 10 identical solutions containing 1% total solids. At the end of the shaking period the non-tannin content of 1 pair of samples was determined in the usual manner. The remaining 4 pairs were each diluted with various amounts of distilled water to correspond to fractional amounts of the original 1% concentration. These 4 pair of samples were then shaken for a further 10 minutes and the non-tannins determined in

TABLE IV

The Equilibrium Between Ligninsulphonates and Hide Powder

Concentration		Absorption by Hide Powder				
Initial	Final	Low Molecular L. S. A	High Molecular L. S. A.	S. W. L.	Purified Quebracho	Xylose
1.0%	——	72.6	42.5	42.3	81.8	nil
1.0%	0.75%	72.3	44.2	39.8	84.7	nil
1.0%	0.67%	72.1	44.2	41.2	——	nil
1.0%	0.50%	71.2	44.2	41.9	83.3	nil
1.0%	0.25%	70.6	44.0	42.3	81.2	nil

the usual manner. The results are shown in Table IV. The constant tannin content of the high molecular ligninsulphonic acid, and the waste sulphite liquor, confirms Gustavson's conclusion that the reaction is irreversible. There appears to be a slight amount of de-sorption in both the low molecular ligninsulphonic acid and in the dialyzed quebracho. Xylose, the predominant sugar present in a fermented sulphite waste liquor, is not absorbed by hide powder. This difference in the absorption of the ligninsulphonates and the sugars by hide powder has been used quite successfully in isolating relatively pure sugar fractions from sulphite waste liquor for other investigations.

The Quantity of Low and High Molecular Ligninsulphonates Absorbed by Hide Powder

Since the ligninsulphonates are irreversibly absorbed by hide powder, it was of interest to determine how much of each is absorbed under saturation conditions. This was determined by carrying out the hide powder test under conditions which were known to give complete absorption, namely 10 minutes at 70°C., and using an excess of the ligninsulphonates. At the end of the shaking period the tanned hide powder was thoroughly washed with distilled water and the non-absorbed material determined in the filtrate and washings. The weight of material absorbed by the hide powder was obtained by difference. Thus it was found that hide powder would absorb approximately 46% of its weight of high molecular ligninsulphonic acid or 23% of its weight of low molecular ligninsulphonic acid. Gustavson [7] has also reported that the weight of the high molecular fraction absorbed by hide powder is twice that of the low molecular fraction, but no experimental details were given.

Non-Tannin Portion of Low Molecular Ligninsulphonic Acid Fraction.

The non-tannin portion of the low molecular ligninsulphonic acid fraction was isolated by absorbing the "tannin fraction" on an excess of hide powder. One litre of solution containing 20 g. of the low molecular ligninsulphonic fraction was stirred for 10 minutes with 100 g. of partially chromed hide powder. The mixture was then filtered and the filtrate containing the non-tannins evaporated to a thin syrup. This was precipitated into alcohol and a white flocculent precipitate filtered off, dried and analyzed. The results are shown on Table III along with corresponding analyses for purified low and high molecular ligninsulphonic acids. The results for the non-tannin fraction are quite different from any lignin fraction previously described. The low sulphonic acid content is probably the reason for its lack of absorption by hide powder. When this material was analyzed for sugars by paper strip chromatography, only a trace was obtained. However, after hydrolysis for 24 hours with normal H_2SO_4 at 100°C., the presence of at least 3 sugars in considerable amounts was indicated. This suggests the presence of a carbohydrate residue which may or may not be combined with the lignin.

Presumably if the lignin had been free, it would have been taken up by the excess of hide powder. The presence of a carbohydrate residue, attached to the lignin, would tend to inhibit its absorption by hide powder.

Summary

1. Sulphite waste liquor has been separated into low and high molecular fractions, free of sugars and inorganic materials, in a ratio of approximately 1 to 2, based on methoxyl content.

2. The low molecular ligninsulphonic acid is characterized by its rapid rate of absorption by hide powder. Within the limits of the Official Hide Powder Test, the effects of time, temperature, pH and concentration are negligible.

3. The high molecular ligninsulphonic acids on the other hand are absorbed very slowly by hide powder and the absorption is dependent to a very appreciable degree on time, temperature, pH and concentration. Thus the Official Hide Powder Test does not indicate the total amount of high molecular ligninsulphonate available for reaction with hide. Under appropriate conditions all of the high molecular ligninsulphonic acid is absorbed by hide powder.

4. Both high and low molecular ligninsulphonic acids are absorbed irreversibly by hide powder, the amount of the high molecular weight absorbed per gram of hide powder being approximately twice that of the low.

5. The low molecular ligninsulphonic acid fraction contains approximately 30% of materials which are not absorbed by hide powder. These materials differ from ligninsulphonic acids in their low methoxyl and sulphonic acid content and in the presence of closely associated carbohydrates.

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7. Gustavson, K. H., Tek. Tid. Uppl. C. Kemi **73**, 59 (1943).

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Effect of Sample Preparation on Precision in the Hide Substance Determination

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ABSTRACT

It is shown that the ALCA method of sample preparation for the hide substance determination (grinding once through a Wiley mill to pass a 4-mm sieve) is inadequate in the case of a chrome-tanned, highly greased upper leather. The precision was significantly improved by additional grinding and mixing, but not by increasing the specimen size from 0.5 gram to 1.5 grams. The probable reason for this latter anomalous observation is discussed.

In order to insure the highest precision possible in the hide substance determination, it seems advisable to pass the sample through the mill several times, preferably using a 2-mm sieve.

I. INTRODUCTION

Previous studies [1], [2] of various modifications of the Kjeldahl method for determination of hide substance in leather showed that the type of leather had a greater effect on precision than the method modifications. In both of the studies referred to, all leather samples were ground in a Wiley mill through a 4-millimeter sieve, and then passed through the mill a second time for additional mixing. It was assumed that satisfactory homogeneity of the samples would be obtained in this way; this assumption was apparently verified by the results, since the precision was found to be the same whether 1.5- or 0.5-gram specimen sizes were used in the determinations. The larger specimens, if the sample was nonhomogeneous, normally would be expected to produce higher precision than the smaller specimens. With vegetable-tanned leathers, the precision generally was higher than with chrome-tanned leathers. Poor precision seemed especially to be associated with a highly greased chrome-tanned upper leather used in a collaborative study [2]. However, when this leather sample was subjected to additional grinding and mixing, the precision was improved and became about equal to that obtained with the vegetable-tanned leather, as shown by subsequent tests made in this laboratory, which was one of the collaborators. It appeared, therefore, that poor precision with this type of leather was due to nonhomogeneity of the sample, in spite of the contrary evidence of equal precision with different specimen weights. Further data on this matter have now been collected and are presented here.

2. EXPERIMENTAL

2.1 *Sample Preparations*

Samples of approximately equal weights were cut from various locations of a side of chrome-tanned upper leather which was high in grease content

(same type of leather as that used in the collaborative test and referred to above). All samples were cut into pieces about ½ inch square and ground in a Wiley mill to pass a 4-mm sieve. The total sample (about 1,000 grams) was mixed on a paper and then divided into four portions of about equal size. The subsequent grinding and mixing of the separate portions were then varied as follows to obtain different sample preparations:

Preparation 1—No further grinding or mixing.

Preparation 2—Preparation 1 passed through the mill a second time (4-mm sieve) and mixed on paper.

Preparation 3—Preparation 1 passed through the mill a second time (2-mm sieve) and mixed on paper.

Preparation 4—Preparation 1 passed through the mill twice (2-mm sieve) and mixed on paper after each grinding.

The four sample preparations were conditioned for several days in a room maintained at constant temperature and relative humidity, and kept there in stoppered bottles until the experiment was completed, all specimens being weighed out in this room.

2.2 *Hide Substance Determinations*

All determinations were made on a six-unit Kjeldahl apparatus. Four samples (replicates) and two blanks were run at one time and constitute a "rack." Four racks, all with specimens of the same sample preparation, were run each day, two of the racks with 1.5-gram specimen sizes, and two with 0.5-gram specimen sizes. When all four preparations had been analyzed in this manner, the process was repeated, giving a total of four racks for each sample preparation and specimen size. The reagents, digestion times, etc., used for the two specimen sizes, 1.5- and 0.5-gram, were those given for Procedures II and III, respectively, in the provisional method for the determination of hide substance in leather[3]. (Procedures II and III differ basically only in the specimen size employed, which necessitates different amounts of reagents, etc.)

2.3 *Results*

The rack averages, together with the standard deviations calculated from the four replicates in each rack, are shown in table I. The averages of all four racks for a given sample preparation of each specimen size are also given, together with the corresponding standard deviations considering the sixteen determinations as replicates. (This is valid as the variability among racks is insignificant.)

TABLE I

Sample Preparation for the Determination of Hide Substance by the Kjeldahl Method

		Preparation 1		Preparation 2		Preparation 3		Preparation 4	
Sample size*	No. replicates	Average % hide substance	S. D.	Average % hide substance	S. D.	Average % hide substance	S. D.	Average % hide substance	S. D.
0.5	4	43.78	0.41	44.08	0.23	44.46	0.13	44.35	0.07
	4	44.38	0.47	44.16	0.11	44.29	0.16	44.22	0.07
	4	44.21	0.44	44.11	0.15	44.35	0.25	44.49	0.20
	4	44.14	0.50	44.37	0.29	44.43	0.17	44.42	0.16
	16	44.13	0.46†	44.18	0.22†	44.38	0.17†	44.37	0.16†
1.5	4	44.19	0.46	44.26	0.18	44.42	0.24	44.30	0.14
	4	44.64	0.54	44.34	0.28	44.18	0.18	44.39	0.16
	4	44.55	0.13	44.18	0.15	44.36	0.20	44.26	0.12
	4	44.45	0.38	44.26	0.16	44.30	0.15	44.30	0.10
	16	44.46	0.41†	44.26	0.19†	44.32	0.20†	44.31	0.13†

Leather: Chrome-tanned upper, high in grease content.
Preparation 1: Ground once through 4-mm sieve, mixed.
Preparation 2: Preparation1 + one additional grinding through 4-mm sieve, mixed.
Preparation 3: Preparation 1 + one additional grinding through 2-mm sieve, mixed.
Preparation 4: Preparation 1 + two additional grindings through 2-mm sieve, mixing after each grinding.

* 1.5-gram samples analyzed by Method II, Provisional Method.
0.5-gram samples analyzed by Method III, Provisional Method.
† All 16 determinations considered as replicates. This is valid as rack-to-rack variability is insignificant.

3. Discussion of Results

From inspection of the results obtained, the following conclusions, verified by statistical analysis, may be drawn:

1. There are no significant differences in accuracy or precision between the two sets of results obtained with different specimen sizes.

2. Two or more grindings (and mixings) improve the precision significantly over that obtained with only one grinding (and mixing). This is true with either specimen size.

3. It is indicated that there is a trend toward highest precision with preparation 4, though the differences between preparation 2, 3, and 4 are not significant.

The most interesting point is that increasing the specimen size is no compensation for insufficient grinding and mixing with this type of leather. Apparently the fibers and particles of the individual leather pieces are not adequately dispersed by the first grinding so that the nonhomogeneity of the original leather is at least partially maintained through the subsequent mixing. The size of the specimen taken from such a sample will not materially

alter the representation of the total sample, since in any case it will consist essentially of a local section of leather.

No doubt the amount of grinding and mixing required for sample homogeneity differs widely for different leathers and is influenced by such factors as tannage and grease content. A sample preparation adequate for all types of leathers should probably be made as in preparation 4, in order to eliminate with certainty a considerable source of error in the hide substance determination.

4. Significance of These Results with Respect to the Provisional Method Recommended by the ALCA Subcommittee

In view of the findings of the present study, it seems necessary for the sake of precision to subject the sample used in the hide substance determination to a finer grinding than that obtained by one grinding to pass a 4-mm sieve. The latter sample preparation, however, is specified for other chemical tests for leathers. The test for water solubles, especially, requires such a sample preparation, and a finer grinding would affect the results in this test adversely. The provisional method for the hide substance determination [3], although based on the results of the collaborative test [2] in which all samples were passed through the mill twice and equal precision was found for 1.5-gram and 0.5-gram specimens, contains procedures allowing one grinding of the sample (4-mm sieve) *provided* 1.5-*gram specimens are used.* It was primarily for the purpose of avoiding the need of more than one sample preparation of leathers analyzed for both hide substance and water solubles that these procedures were included. The assumption was made that the lesser grinding and mixing of the sample would have a neglible effect on precision when the larger specimens are used. The results of the present study show that this assumption is not valid and it is recommended that the sample preparation of the provisional method should be revised accordingly.

5. References

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Acknowledgment

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ABSTRACTS

Report of (French) Consultative Commission on Leather Research Techniques. *Bull Assoc. Franc. Chim. Inds. Cuir.* **13,** 21 (1951). (1) Discussion on the report on salting tests on calf-skins made at the Leather Research Institute. (2) Discussion on the report of the International Research Institute for the Improvement of Raw Hides and Skins. (3) Future requirements for waterproof upper leather destined for the (French) Army Service Corps, and discussion. A. N. K.

Study on Unhairing. By P. Chambard and I. Julien. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 27 (1951). Alternate halves of two croupons were limed in 2 series of limes, each series being made up with the same lime and sulfide concentrations, but the one being held at 15°C and the other at 30°C. Four such tests were made. In each case, liming was stopped as soon as the hair was easily removable on the beam. Sulfide and Total Alkalinity of the liquors were determined before and after liming, and dissolved protein after liming. After liming, the stock was washed and then delimed with ammonium chloride and hydrochloric acid and then tanned in liquors of sweetened chestnut, starting at 1°Be and pH 5.3, and finishing at 6°Be and pH 4.8. The stock was rinsed, scoured and dried, then wet back, set-out, milled to even the moisture and weighed. A sample was cut from the shoulder for moisture determination and the weights of all croupons then calculated back to 70 per cent moisture. The hide substance content of the delimed hide had been determined and the total weight thereof calculated for each croupon on a 70 per cent moisture basis. The finished leathers were weighed and analyzed and all calculated to 14 per cent moisture. The data are listed in Tables. It is concluded: (1) Increase of temperature increases rate of unhairing, that at 30°C being double that at 15°C. (2) Dissolved protein increases with increase of temperature; this does not necessarily represent loss of hide substance. (3) While difficult to obtain accurate yield figures on such small tests, the results suggest no actual yield loss at the higher temperature, with the shorter time. (4) It is proposed to determine the hydrolyzing power of warm limes more rigorously. A. N. K.

Mode of Operation of the Method of Direct Detannization. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 35 (1951). A contribution from the Lyons Institute of Leather Research. Into a 250 ml, wide-mouth, conical flask introduce a weight of Hide Powder "for direct detannization," equivalent to 6.25 g. of dry material; add 100 ml. of analytical solution, close the flask with a rubber stopper and shake mechanically for 20 minutes. Stand 10 min. Previously arrange a filter apparatus composed of a funnel with fritted glass filter, corresponding to Pyrex No. 172.211, fixed to a 200 ml. filter flask with a rubber stopper, and connected to a source of suction through a safety flask. Prepare the filter bed by starting a slight suction and pour the hide powder and detannized solution onto the fritted glass. Lightly and progressively squeeze the hide powder on the plate until slightly dry, using the rubber stopper from the shake bottle. With extracts and usual tanning materials there is no advantage in squeezing too hard as that gives too dense a filter and needs too strong a suction later. Disconnect the filter flask and pour back the cloudy filtrate, as completely as possible, into the shake bottle. Rinse the filter flask with 3 consecutive filtrations by pouring about 20 ml. of the detannized solution through the hide-powder filter. By this time the filtrate should be perfectly clear. At no time allow air to pass through the hide-powder. Finally, a last filtration is made under the same conditions and with the same care (presumably, repouring the whole of the detannized solution through the filter—ANK). About 70 ml. of clear filtrate will be obtained and 50 ml. is evaporated and dried. The residue represents the nontans in 50 ml. of analytical solution. A. N. K.

Phosphate Tannage in the Manufacture of Vegetable Tanned Leather. By C. Riess. *Rev. Tech. Inds. Cuir.* **43,** 26 (1951). The history and basic principles of phosphate tannage are discussed. Commercial metaphosphates ("Coriagin" and "Calgon") are polymers, mainly the hexa-polymer but containing others of higher molecular weight. Like the auxiliary syntans, they do not produce a marketable leather so are usually used in combination, especially as a pretannage. By thus protecting the hide from too-rapid fixation of tannin, strong liquors may be used, thereby avoiding the losses usual to ordinary weak liquors while obtaining rapid penetration and avoiding drawn-grain or case-hardening. The phosphate is progressively displaced by the tannin in the later stages of tannage. These advantages alone would not justify the high cost, but such leathers have a clear and uniform color and good physical properties, especially tensile strength and grain-elasticity. The improvement in color is due to the strong sequestering action of the metaphosphate for, particularly, iron and calcium. The increased grain-elasticity is probably due both to this sequestering action and to the low pH used. The maximum absorption of phosphate is at pH 2.2-2.3 which involves a thorough washing after pretannage. Today, phosphoric acid is used to adjust the pH of both the pretannage and the tanning liquors. During the war, the necessity of using blends high in Spruce Bark extract resulted in a reddish leather and inhibited tannin penetration. "Coriagin" at pH 3-4 immediately eliminated these difficulties and, at these pH values, less phosphate was needed and the thorough washing after the usual pretannage was avoided. A. N. K.

Synthetic Resin Adhesives. By P. Gourlay. *Rev. Tech. Inds. Cuir.* **43,** 27 (1951). *General:* Adhesives are used to form a solid bond between two materials, and must not only adhere to the surfaces to be joined but must possess good cohesion within themselves. In some cases, adhesion must be only temporary, as in the pasting of leather. *Nature of Adhesiveness:* is discussed and indicated to be due to those intermolecular forces which only act over a short distance from the surface. Two perfectly smooth surfaces can be "wrung" together but the difficulty of producing such surfaces and the ease with which they become coated with a film of gas, water, oxide, etc., render such a procedure unfeasible. Since a film of liquid helps to level surface inequalities and eliminates the effect of the surface film, most adhesives are liquids or behave as such. However, the nature of the surfaces and of the adhesive determine the effectiveness of the bond and this is indicated as being due to the polar nature of the components; the strongest bonds are formed when both surfaces and adhesive are of the same polar type. Examples are given. There is a certain parallelism between the affinity for water and the polar type—hydrophilic substances usually being polar, hydrophobes non-polar. Dextrin, starch, gums and glue are strongly polar, casein is less so, while natural and synthetic rubbers are non-polar. Certain types of synthetic resins, of intermediate polarity, are the best, general, adhesives. *Properties Required of Adhesives:* (1) Maximum bonding force; (2) Minimum drying time; (3) Ease and Speed of Application; (4) Ability of the bond to withstand the tensile and flexing stresses of the particular junction and to remain permanent over long periods under unfavorable conditions; (5) Economic in use; (6) Small increase in cost; (7) Good storage characteristics, and uniformity and regularity from batch to batch; (8) Lack of health hazards, particularly where solvents are involed; (9) Will not corrode, discolor or change the color of the materials on which used. The majority of synthetic resin adhesives fulfill these conditions, but price is high. Recent developments in the science of adhesives and increased knowledge of their polar properties have resulted in mixtures of various resins in suitable solvents which form very strong junctions with a variety of materials, the joints, properly made, being stronger than the material itself and, in many cases, more durable and cheaper than sewing, rivetting or soldering. Polar adhesives are usually

applied in aqueous solution. Of the non-polar types some, e. g., phenol-formaldehydes, are applied as thin films which liquefy on heating and form the bond on cooling; others, as solutions in suitable organic solvents; others, e.g., urea-formaldehydes, in aqueous solution in which they are soluble until warmed, especially with a catalyst. Mention is made of adhesives in the form of O/W-type emulsions and their advantages: (1) Avoidance of inflammable, toxic, odorous and high-priced organic solvents; (2) Easier application onto, and better penetration into, polar surfaces. In a subsequent paper, the more usual types of resin adhesives—phenol-formaldehyde and melamine resins, acrylic cements, glyptals, and those based on formo-phenolic, formo-carbonic, and formo-resorcinic resins—will be discussed. The properties of the three last have been studied by J. de Buigne (Rev. Tech. Prod. Chim., Dec., 1947), and copies of his paper will be sent to anyone interested. (to be continued.) A. N. K.

A Productivity Campaign Which Has Borne Fruit. By "P. G." *Rev. Tech. Inds. Cuir.* **43,** 30 (1951). A description of changes made in the "ROC" shoe factory at Autun where, by the use of labor- and effort-saving devices, of incentive pay, and of a reduction in the number of models, production has increased 50 per cent, wages have risen 20 per cent, and the price of shoes has not risen despite a 15-20 per cent increase in cost of raw materials. In general, adaptations of principles common to American shoe factories have been used and the results bear out these principles: (1) If physical effort is suppressed, speed is not tiring; (2) the "Robot", which continually carries out one given operation, has been replaced by intelligent workmen who improve their output; (3) The manager, by setting up best working conditions and minimizing fatigue, and the workmen, by their skill and cooperation, combine to keep production and wages high and costs low. This factory now produces 5 pairs per workman per day, against the national average of 2 pairs and the American average of 8 pairs. Further improvement is expected. One operation not seen in America, by which all the parts of a complete shoe upper are cut out in one blow of a die, has been patented. A. N. K.

Report of the Hide Powder Commission. By M. Parsy. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 46 (1951). (1) Hide Powder EFT5, found suitable earlier, was declared Official. (2) Comparison was made between the American Official No. 25 and the EFT5 Hide Powders. It is concluded that the two powders are sensibly the same as far as soluble matter and detanning action are concerned. (3) A sample of the American Official Kaolin was obtained and is to be compared with that of the A.F.C.I.C. It is hoped that these results will be of value to the International Commission. Members were also circularized to learn their ideas on a project to determine the conditions for International admission of White Hide Powders. A. N. K.

Dyeing of Leathers Tanned with Synthetic Tannins. By Ch. Faure. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 47 (1951). This study was undertaken because of the increasing use of syntans either alone or in combination with vegetable or chrome, not only for skins to be finished white or natural but also for those to be dyed or colored. The most difficult dyeing problems relate to Direct Tan, Glace, and Direct Suede. In these, the skin is chrome-tanned, neutralized, rinsed, and mordanted with vegetable (gambier or sumac) or synthetic tan or mixture of both. Then fatliquored with an emulsion high in wetting and emulsifying agents. This permits of easy rewetting prior to dyeing. While the affinity for basic dyes is increased by the vegetable, and especially so by the synthetic tannin, the

same is not true with acid or direct dyes which fix poorly or not at all on synthetic-tanned leather. For such dyes, syntans act as retarders and give clear shades. However, there are dyes which have an excellent affinity for syntanned leather. While, due to their phenolic –OH groups, vegetable tans are feebly electronegative, the presence of $-SO_3H$ or of $-CH_2OSO_3H$ groups in the syntans makes them markedly so. Vegetable tannins, treated with $NaHSO_3$, are intermediate. Treated with these materials, the hide assumes a similar electronegative character. When chrome-tanned, the hide becomes electropositive, the degree of positivity being diminished by anions, and especially so by masked, chrome complexes. Dyeing is considered a lake-formation and the charge on the leather will determine the type of dye fixed. Thus, chrome leathers generally have a strong affinity for acid or direct dyes; vegetable leathers have a strong affinity for basic dyes but, their negative charge being low, they have an affinity for some acid dyes. Syntanned leathers have a very strong affinity for basic dyes and none for acid dyes, except for those whose colored anion has a low negative or basic character. Based on this hypothesis, the following points were studied with several dyestuffs (formulae given): (A) *Influence of Sulphonic Groups* (1) those with one or two sulfonic groups fix on syn-tanned leather, while those with three or more do not fix. (II) the position of the sulfonic groups does not seem to have any effect on fixation; (B) *Influence of NH_2 or OH groups:* Much less noticeable than effect of sulfonic groups, though those containing NH_2 are slightly superior to those with OH; (C) *Influence of Structure:* While the triphenylmethane dyes have a very strong affinity for syntanned leather, often precipitating on the surface, this is probably due to their basic character rather than to their structure. Since fixation is a matter of the electrical character of the leather and dyestuff, materials which combine with electronegative groups on the hide, thereby neutralizing them, increase the affinity of vegetable and syntanned leathers for acid and direct dyestuffs. By adjusting the conditions, the dyestuff can be made to penetrate or to remain on the surface. It is pointed out that the ionic character of all materials entering into the formation of the leather will have a similar influence on the fixation of dyestuffs. A. N. K.

Chromatography Applied to the Qualitative Analysis of Tannins. By H. Martin. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 58 (1951). Chromatographic Alumina (Prolabo) was used as absorbent, aqueous methyl alcohol as solvent for the tannin, and ethyl acetate as eluent. Grassman's procedure of packing the dry absorbent into a tube 7.5 mm. diam. by 16 cm. long, the bottom being closed with a wad of cotton-wool and a 1-hole stopper, and using 2 ml. of the tannin solution followed by 3 to 4 ml. of ethyl acetate, gave capricious results attributed to the difficulty of obtaining a uniform column and to variations in the fineness of the alumina. The latter was overcome by using what was retained on a No. 25 sieve (0.067 mm.); the former, by using a wider tube and filling with a suspension of alumina in the solvent, the upper level of which was never allowed to go below the surface of the alumina. Uniform packing could be achieved by centrifuging the tube, but was inconvenient and reduced the number of tubes which could be handled at one time. The procedure adopted was to reject the alumina which passed the No. 25 sieve, and to use Pyrex tubes 15 to 16 mm. diam. by 12 cm. long. Each tube was closed at one end with a rubber stopper through which passed a 5 mm. glass tube fitted with stopcock, the upper end of this tube being flush with the upper surface of the stopper. A layer of waterproof cotton or glass wool was placed on top of the stopper to cover the opening into the small tube. Dry alumina was poured into the large tube to a height of about 8 cm., without tamping, (about 20 g. of alumina). The alumina was then emptied into a small beaker and wetted with a mixture of 10 ml. methyl alcohol and 5 ml. distilled water. The stopcock being closed, the well-mixed suspension was poured into the tube, held vertically, and

allowed to stand 10-15 minutes to settle. If the level of solvent were below the surface of the alumina, more solvent was added. Open the stopcock until the level of solvent is about 1 mm. above the surface of the alumina. A 14 per cent (approx.) aqueous solution of the tannin is prepared and about 5 ml. taken, mixed with an equal volume of pure methyl alcohol, and filtered. 3 ml. of the filtrate is then carefully added into the top of the prepared tube so as not to disturb the alumina. Open the stopcock until the solution level is again about 1 mm. above the alumina surface. At this stage, it will be found that the absorption, colored in the case of most vegetable tannins, extends some 2-3 cms. down the column. In ordinary light, there is often a distinct ring at the limit of absorption and of a distinctive color; under U. V. light, this ring will often show a distinctive fluorescence. 6 ml. of ethyl acetate is then carefully added in three or more portions, and the solution allowed to pass until the level almost reaches the alumina surface. It is sometimes useful to observe the column under U. V. as elution proceeds; with quebracho, the substance fluorescing strongly yellow can be observed to descend some 2-3 cms, there forming a ring about 1-2 mm. thick with a very intense and characteristic fluorescence. The elution completed, the top of the tube is closed with a rubber stopper and it is best to leave the stopcock open to avoid solvent-migration. Since the chromatograms fade quickly, they should be examined under U. V. light as soon as possible and not later than the next morning. Three absorption zones can usually be seen under U.V.: (1) At the top, a zone of different shades of brown, more or less uniform and more or less dark or luminescent; (2) Below the above, a more or less narrow ring, having a fluorescence often characteristic and more or less intense; (3) Finally, a luminescent zone in different shades of blue or violet. A table is given showing the results obtained on Quebracho, Urunday, Wattle, Chestnut and Oak. Some pure extracts give very distinctive chromatograms while others are very similar to each other. Lignosulfonates do not give a distinctive chromatogram. Syntans are distinctive and those containing only phenols may be distinguished from those based on naphthalene. In mixtures, the results are far less definite, the zones characteristic of each tannin being irregularly modified by the other components. Hence, at this stage, the identification of mixtures cannot be made with certainty so that the more usual qualitative tests must first be applied, when probable (known) mixtures can then be prepared and compared chromatographically. The possibility exists, however, that the sequential use of different eluents may eventually permit more exact evaluation of mixtures. A. N. K.

Antiseptics and Germicides in the Leather Industry. By U. J. Thuau. *Rev. Tech. Inds. Cuir.* **43,** 41 (1951). The increasing use of antiseptics and germicides in all stages of leather manufacture, from raw hide to finished leather, is indicated and the terms antiseptic, disinfectant, germicide, bactericide, insecticide, etc., are defined. An instance is given of how losses in soaking can be prevented by using 0.05 g. of parachlormetacresol per liter of soak water. (to be continued.) A. N. K.

What Is Wool. By I. W. S. *Rev. Tech. Inds. Cuir.* **43,** 44 (1951). This paper is a reproduction "in extenso" of an article appearing in "Nature", January 1951. Of the 34 amino acids occurring in nature, 17 are found in wool, and their proportions are illustrated graphically. Unlike silk, in which the scarcity of side chains permits the polypeptide chains to come very close together, wool contains many side chains so that the polypeptides are widely spaced. Salt-links, formed between $-NH_2$ and $-COOH$ on adjacent side chains, and especially the sulfur-containing cystine which forms sulfur bridges between main chains, give wool its resistance. There are other, weaker, attractions such as hydrogen bonds, etc. Thus wool can be considered as a series of layers formed of long polypeptide chains bound by various transverse bonds; the layers being superimposed on each

other and spaced and united by hydrogen bonds between peptide bonds of adjacent chains. The length of individual polypeptide chains is difficult to measure and they probably vary from 60 to 400 amino-acid residues before terminating with a –COOH or–NH_2. The arrangement of the amino-acids along the chain is also difficult to determine and can only be approached by careful degradation to di- and tri- peptides which can then be analyzed. Results to date indicate that, if any order exists, it must be complex. Keratin of wool is reactive and its properties can be changed by treatment. Acids tend to combine with amino-groups and, at low concentration and tempreature, their action is weak and reversible. Under more severe conditions, they destroy the amino-group and attack certain amino-acids such as tyrosine. Dyeing with acid dyes is difficult. Alkalis break the salt links, the disulphide links, and the cystine, and excess weakens the fiber and diminishes its elasticity under stretch. Bleaching by oxidizing agents acts mainly on the disulphide bonds. Lessening the shrinkage or felting of wool has been attempted by treatment with chlorine or its compounds but these attack the disulphide bonds and probably some of the peptide chains also. Steam and sunlight are not without action. The disulfide bridge is unstable and any damage causes lowered resistance to wear, to swelling, and to chemicals, and alters the color and feel. Attempts to overcome this have been directed to forming new transverse bonds and to modifying the disulfide bonds. Formaldehyde reacts with amino-groups to increase resistance to alkalis, and temporarily inhibits shrinkage, but the new bond is unstable to acids and to boiling water. Reduction of the disulfide bond gives two cysteine residues, when treatment with a polyvalent metal or with halogenated compounds gives a much more stable bond. With ethylene dibromide, a thio-ether bridge is formed. This strengthens the fiber and confers stability to thread and cloth. To date the only application has been in a non-textile industry—the waving of hair. A. N. K.

New Method for Measuring the Permeability of Leather to Water Vapor. By L. G. Davis. *Rev. Tech. Inds. Cuir.* **43,** 47 (1951). The need for such a method, especially for shoe-uppers, is indicated. The rest of the paper appears to be a rather full abstract of that of Kanagy and Vickers, LALCA. **45,** 211 (1950). A. N. K.

Sampling of Leather for Shoe Uppers. By Anon. *Rev. Tech. Inds. Cuir.* **43,** 51 (1951). Appears to be an abstract of the paper by C. W. Mann et al, published a month later in JALCA. **46,** 248 (1951). A. N. K.

The 'Ansul' Method for the Production of Chrome Liquors with Sulfur Dioxide. By P. G. *Rev. Tech. Inds. Cuir.* **43,** 53 (1951). A description of the method recommended by the Ansul Chemical Co., for the economical and simple preparation of constantly uniform chrome liquor. Present equipment can be used by fitting the dissolving tank with a dispersing spider at the bottom and providing means for measuring and regulating the introduction of the SO_2. Typically: Into a 500 gal. lead-lined tank, add 950 lbs. of crystal sodium dichromate and 475 gals. water. The SO_2-control valve is opened wide and 590 lbs. of SO_2 admitted through the spider. Due to the reaction:

$$Na_2Cr_2O_7.2H_2O + 3SO_2 \longrightarrow 2CrORSO_4 + 2Na_2SO_4 + 2H_2O$$

considerable heat is generated and the temperature will rise to 200°F, and the liquor will smoke. Close the valve and slowly add about 22 lbs. more SO_2, testing frequently until reduction complete. The basicity will then be exactly 33⅓ per cent. Steam is then passed for 1½ hours to remove any excess SO_2, and to ripen the liquor. Dilute to 500 gals., cool, and add the required amount of the desired masking agent. During the final, slow addi-

tion of SO_2, the progress of the reduction can be followed simply by diluting a drop or two of the liquor with water in a test tube and observing the color; this changing from greenish-yellow to greenish-blue. When only a slight additional change is evident, resort is had to the starch test: put 1 ml. of 5 per cent starch solution and 1 ml. of 10 per cent KI solution into a test tube and add 10 ml. of dilute HCl (20 ml. conc., diluted to 1 liter). Add 1 drop of the chrome liquor and shake. A blue color indicates presence of unreduced chromate. When no color is obtained, the SO_2 is shut off and the steam turned on. Various precautions are indicated. Fuller details may be obtained from the Ansul Chemical Company. A. N. K.

Synthetic Resin Adhesives. By P. Gourlay. *Rev. Tech. Inds. Cuir.* **43,** 55 (1951). The second of two parts. *Phenol-formaldehyde,* or formo-phenolic, glues are usually applied in aqueous solution and are particularly valuable for the glueing of wood, and in producing plywood. They are obtained either as easily water-soluble powders, or in admixture with a high proportion of blood or other protein, or as liquids. Cements based on a mixture with rubber are air-drying, and of value where quick-drying and a flexible film is needed. A formula and instructions for preparation are given for a type used in Germany in 1944. Mixed with a hardening agent and powdered silica or quartz, a mastic for cementing brick is obtained resistant to non-oxidizing acids but not to alkalis. *Formo-carbamic and Formo-melamine* resins are produced by spray-drying the syrup obtained by mixing urea or melamine with formaldehyde. The powder is quite stable and easily soluble in water to give a viscous liquid. During setting, the pieces to be joined should be clamped. Cold-glueing with the formocarbamates may be accelerated by using hardening agents. The formomelamines require heating to 90°-100°C and will then resist boiling water. To obtain proper elasticity, additions are made: powdered plaster, up to equal amount, is used but weakens the joint; rye flour is also useful; vetch flour can be used up to 300 per cent without lowering the resistance of the glue to dryness or humidity. By the addition of acids weaker than phosphoric, together with buffers, hardening can be delayed up to 48 hours and, during the first 12 hours, manipulation of the joint is possible, thereby increasing the utility. Hardening agents are chosen according to whether operating cold or hot. In the former, phosphoric acid or ammonium chloride is used; in the latter, solutions of urea and of ammonium chloride, with ammonia as buffer. The formo-carbamates are easier to use. *Formo-resorcinic* resins have the advantage of hardening at ordinary temperatures and under neutral conditions, thereby avoiding attack on the fiber. The joint resists boiling water, weak acids and alkalis and many solvents. The prepared solution is usable for several hours. U. S. Pat. 2,585,730 (cited) gives information on the preparation and method of using this type of resin, which is valuable on wood or natural or synthetic rubber. It is also used (U. S. Pat. 2,385,371) for making sandpaper. *Urea-based* resins are obtained by warming together urea or thiourea and formaldehyde or other aldehyde. They are pale in color and can be colored with light tints. They are non-flammable, resistant to atmospheric influences and to weak acids and alkalis (pH 6 - 8.4), alcohol, acetone, oils and fats. The catalyst is usually a weak acid or salt of a strong acid. In many cases, greater economy can be effected by use of extenders such as rice flour. They are sometimes alkyd-modified. *Polyvinyl cements:* the acetates, chlorides, and butyrates of polyvinyl, or their mixtures, have remarkable power of adhesion to a great variety of porous and non-porous surfaces. *Acrylic Resin* cements are used to a large extent as impermeable barriers for a variety of materials. The Acryloids and Acrysols are the most interesting and their characteristics depend on those of their monomers. The former are colorless and transparent, have high adhesivity, elasticity, chemical resistance, durability, and stability to heat and light. Usually modified with 15-20 per cent of plasticizer, such

as a mixture of dibutyl sebacate and phthalate, and 15-20 per cent of cellulose nitrate. The Acrysol is a 25 per cent solution of resin in water and is compatible with latex, and is particularly useful for cementing rubber to rubber-surfaced materials. *Other Adhesives and Formulae: Chlorinated Rubber* is non-inflammable, stable to 125°C, and soluble in many organic solvents, in linseed and other vegetable oils, and in some plasticizers. Formulae for two adhesives are given. For cementing shoe soles, various synthetic rubber cements are used. A formula is given for a polyvinyl cement resistant to water, acids and oil. Mention is made of a glue obtained by mixing an acid, an aldehyde, and an amine or amide; formula given. Mention is also made of other cements, including mixtures of resins and hide-glue. *Pasting Adhesive for Leather:* the difficulty encountered and factors responsible are indicated. "Clear Flo" is the sodium salt of a partially modified and ungelatinized starch and is said to be particularly valuable for pasting. The characteristics of this American material, and methods of using same, are detailed, and the effects of acids, alkalis, and salts is indicated. A. N. K.

Study on the Conservation of Calf Skins in the Hair. By MM. Vourloud and Desjours. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 75 (1951). Nineteen sets of 16 skins each were subjected to different conditions of salting, such as variation in time of salting after slaughter, amount of salt used, washing before salting, treatment with one of four antiseptics (Merpin W.S. Extra 40; Steripo; S.54; $Na_2S_2O_5$), either before salting or in admixture with the salt. The packs were then divided and four hides were bundled immediately and put into pile while another four were piled flat and allowed to drain: for 3 days in the case of those in which antiseptic was sprayed on, and for 6 days for those merely salted. The piles were covered all over and surrounded with bags of salt. Some desiccation occurred, despite these precautions. The odor and characteristics of the antiseptics are given as well as their effect on working conditions. The piles were examined at the collector's plant, after receipt at the Institute, and at other stages through the process of tanning and finishing. Temperatures attained in the piles, and the analysis of the salt are listed. In examining the stock, the following defects were sought: Red Coloration of the flesh; Brown stains on the flesh; Violet stains on the flesh; Salt stains and Green arborescence on the grain; Grain pricks; White stains on the grain. The finished skins were tested for grain crack by the "key" test. The skins were tanned into box and the quality of the leather evaluated. Tables are given showing the results of the several examinations, from which the following observations were made: (1) It is necessary to salt as soon as possible after slaughter; (2) The red stain increases as the skins hold more brine or more salt lies between the skins; it increases with the handling of the skins and masks salt stains on the flesh which only reappear after soaking; (3) The green arborescence of the grain is generally produced in a frequently-renewed atmosphere and generally appears only after liming; (4) Salt pricks on the grain are characteristic of skins not drained before being bundled; (5) Washing the skins with running water before salting is a dangerous operation but the quality of the leather (ignoring conservation defects) is excellent. This is to be restudied; (6) Certain stains, observed in the white, disappear after tannage but reappear at the finish; (7) An excess of salt is as bad as too little; (8) Generally, the antiseptics have the defect of giving the flesh a light-brown color with spots of deeper brown in the region of the blood vessels. However, especially on skins drained before bundling, they give box with finer grain, rounder feel in the flanks, and which are less ribby; but some skins show a greater number of grain-cracks under the key test. None are completely devoid of fault of one sort or another. Metabisulphite does not give grain defects but the leather is more "open". Where an antiseptic produces coagulation at the time of salting, there is a greater tendency to green arborescence on the grain. A program

for future studies is indicated, this to include analyses and microbiological examination of the brine draining from the skins before bundling. A. N. K.

Congress of the International Society for the Improvement of Leather and Raw Skins. By H. Vourloud. *Bull. Assoc. Franc. Chim. Inds. Cuir.* **13,** 88 (1951). This report was presented at Turin on October 8 and 9, 1950, by Dr. Gannsser. The organization of the society is detailed. The main work presented was that of M. Gregoire of the Belgian Society who had studied the Warble fly. There are two flies (Hypoderma Lineatum and H. Bovis) which differ in their jaws, those of H. Bovis being more powerful. The larva of H. Lineatum is found in the submucous of the aesophagus but never in the latter itself, and it is supposed that the larva proceeds via the salivary glands. It develops in the submucous to a certain degree and then moves to the dorsal region. H. Bovis, however, is always found in the spinal canal and it is supposed that the larva goes there directly. Tests were made with various insecticides, either as powder or in solution, at various concentrations. Of these, rotenone was the best; it was found that optimum results were obtained by making three applications (March, April and May) of a 2 per cent solution of rotenone in water to which was added a wetting agent, together with CO_2 to prevent the rapid destruction of the rotenone by oxidation in alkaline solution. In Belgium, the Tournai region is most afflicted and flies are active from March to July. However, the development curve of warbles shows maxima in May and July, and these were shown to coincide with the development of H. Lineatum and H. Bovis respectively. Properly applied, the above rotenone solution showed a 98 per cent reduction in warbles on the treated cattle compared with untreated controls. No vaccine has yet been developed against the warble. All breeding farms in the Tournai area where affected by warble except one which remained absolutely free, although the cattle were treatd no differently from those in the neighborhood. The reasons for this are being investigated. A. N. K.

Antiseptics and Germicides in the Leather Industry. By U. J. Thuau. *Rev. Tech. Inds. Cuir.* **43,** 64 (1951). Second of a series. This deals with the germicidal power of antiseptics and germicides and, especially, means of comparing their effects. The Rideal-Walker method is detailed, and the R-W values of some materials are listed, including some collected by J. A. Wilson from Thorpe's Dictionary of Applied Chemistry. Vago's method, used by Wilson in studying finishes, is also detailed. In this method, varying amounts of the materials under test are added to aliquots of a 40 g. per liter solution of casein at pH 7 maintained at 25°C., and the time required for onset of putrefaction is noted. Values obtained by this method are given for some materials. A. N. K.

Aims and Diverse Phases of Beamhouse Work and Practical Means of Attaining Them. By A. W. Goetz. *Rev. Tech. Inds. Cuir.* **43,** 66 (1951). An address given to the New England Tanners' Production Club in January 1951. *Hide Store:* the importance of proper humidity control, if uniformity in subsequent processes is to be attained, is indicated, and the desirability of soaking skins of the same thickness, rather than of the same weight, is stressed. *Soaking:* this is probably the most important of all. Its purpose is to rehydrate the skin to as near its original condition as possible, and to remove materials such as the globular proteins whose presence stiffens the leather. By suitable addition of salt or of polysulfide, time and material may be saved in the liming, oiling and staking. Disinfectants are of value as they permit of higher temperatures which then allow of the use of enzymes as accelerators. *Liming:* the chemical and physical changes, initiated in the soaks, become more pronounced in the limes, and the lime is the important agent. However, as

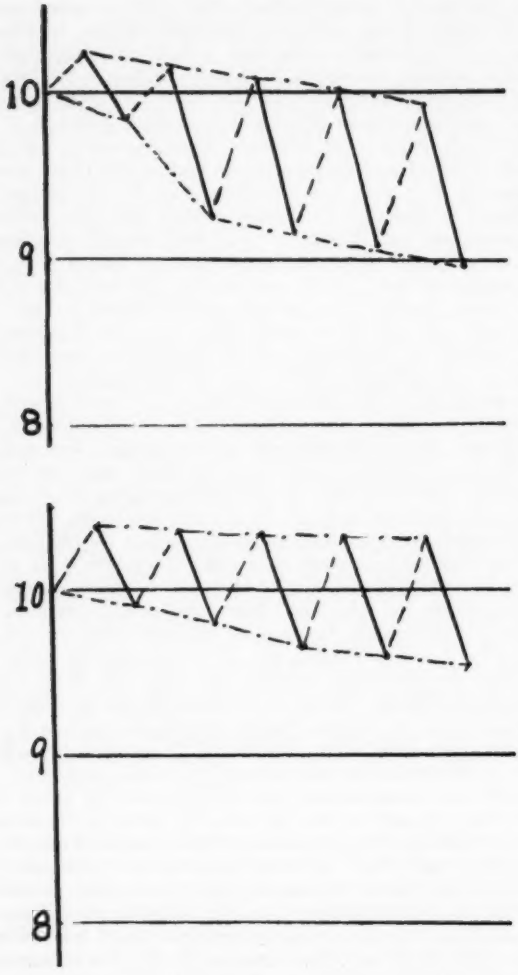
the lime is the most important problem in waste-disposal, other materials should be sought. While lime is the base material, it is the sharpening agent which controls the swelling, the loosening of the hair, and the appearance of the grain. Fresh lime "immunizes" the hair so that the sooner the unhairing agent is added the better. Uniform distribution is most important and intermittent mechanical action is suggested. Controlled immunization can be helpful: whereas placing the skins into a lime containing 2 per cent of double-strength sulfide would decorticate the hair, immersion of the skins in a fresh lime for 6 hours and then adding this amount of sulfide allows the hair to be recovered in two days. Besides removing the hair, liming modifies the protein and gives mellowness and suppleness to the stock; the longer the liming and the higher the temperature, the softer the leather, the more united the grain and the more the skin is extended. *Bating:* depending on the amount of washing after liming, the stock will contain more or less lime so that the first action of the bate must be a continuation of the liming action at the higher temperature. As the deliming salts lower the pH, the enzymes begin to act to remove keratose and other degraded protein. When using a fermented dung bate, the stock was only surface-delimed; while this was thought to be necessary to prevent bacterial action, there is little doubt that there was considerable hydrolysis by the lime. Using non-fermenting bates, in two baths, the flattest grain and best spread-out stock is obtained when the pH of the first bath is 9.6-9.8 rather than 8.0-8.3. Also a smoother grain is obtained when the washing before bating is reduced to a minimum, while high grain is produced if the stock be first completely delimed to phenolphthalein. By suitable control of the washing and of the deliming agents used, this desirable hydrolysis can be controlled. For best results, therefore, a definite and controlled volume of water at a definite temperature should be used for the washing prior to bating, and this also saves water. Washing after bating should be similarly controlled as the amount of lime carried forward affects not only the acidification of the skins in the pickle but also the distribution of the acid and, subsequently, the degree of tannage and acid-distribution in the leather. It is suggested that the bate be emptied, the paddle refilled with water at 75°-80°F. and wash 5 minutes. The usual practice of paddling intermittently during bating has important effects on the grain and aids diffusion of material into and from the stock. Bacterial are not as effective as pancreatic enzymes but this may eventually be overcome. It is felt that the enzymes increase the speed of deliming, the pancreatic more so than the bacterial. Many major tannery problems are the result of the ignoring of small but cumulative details, lack of consideration for which is one reason why we do not have full control of process. A. N. K.

Rapid Method for Dyeing Furs. By M. Bogaewski. *Rev. Tech. Inds. Cuir.* **43,** 70 (1951). The usual dyeing of furs with "Fouramine" dyes requires four operations: viz., pickling, tannage, mordanting, dyeing. The proposed method requires but three: pickling and mordanting being combined. Dyeing may follow immediately thereafter, followed by tannage (in which case the tannage (?) may be made by dipping or brushing) or the tannage may precede the dyeing. In the first case, any type of tannage may be used but, in the latter, the tannage must resist water (chrome or syntan). Application to sheepskins in black, brown or seal is illustrated with formulae. Not only is the process more economical, but skins tanned after dyeing are better resistant to rubbing and lose their color less easily. Also, the leather is scarcely colored, which permits of imitating natural furs more exactly. However, it is not possible to sort the skins between tanning and dyeing. A. N. K.

The Shrinkage of Insole Leather Under the Action of Sweat. By W. Grassmann and P. Stadler. *Das Leder* **4,** 218 (1953). Insole leather, in addition to good flexi-

bility and high tensile and tear strength, should possess a high ability to absorb water. When moist it must give up neither mineral matter nor uncombined tannin. Of primary importance is its resistance to foot perspiration which tends to make the leather dark in color, hard, horny and low in strength and stretch. Before the leather is damaged by sweat, there is a change in shape caused by expansion of the insole when damp and contraction when it dries. The stability and shape of the shoe then suffers, especially if the shoe has a rubber or synthetic sole which is not influenced by wetting and drying. Previous investigators have been concerned with the chemical composition and physical properties of deteriorated insoles, but have given little consideration to the real problem of "change in length" or shrinkage of insoles. Natural sweat contains, principally, ordinary salt (0.3-0.5 per cent), somewhat less urea (0.1-0.2 per cent), small amounts of inorganic salts (phosphates, sulfates, etc.), organic acids and traces of fat and protein from hide decomposition. Freshly secreted sweat has a weakly acid reaction (pH 5-6); this acidity is not harmful to leather. Sweat, however, is a favorable culture medium for bacteria. Among other reactions, the urea is decomposed by urease, which is present in abundance in bacteria, to ammonium carbonate or to ammonia, whereby the sweat becomes alkaline in reaction. Direct damage by urea, although possible, plays no important role in insole deterioration. Of primary importance is the alkaline reaction of the sweat altered by bacteria. The shrinkage behavior of leather under repeated action of artificial sweat and drying was determined as follows: Squares of leather, 10 + 10 centimeters, were used to avoid orientation effects. The average length of a side was measured by taking the length of each of the 4 sides exactly 1 centimeter from the edge, then averaging the 4 values. The artificial sweat solution contained 1 per cent salt, 0.6 per cent ammonium carbonate, 0.2 per cent dipotassium acid phosphate, and sodium hydroxide to adjust the pH value to 9.0. After measurement of the leather it was submerged for 24 hours in 150 cc. of sweat solution at 35°C in a flat covered dish. It was then lightly rinsed, dried on the surface, aired 1 hour, and measured to give the wet dimensions. Next it was dried for 24 hours at 65 per cent relative humidity and remeasured. Observations were also made for curling, hardening and discoloration. The soaking and drying was repeated 4 times for a total of 5 immersions. The results were then plotted with average length of the side of the specimen as ordinate and treatments as abscissas. The scale was chosen so that 2 centimeters (cm.) on the chart represented 1 cm. of specimen length. On the abscissa axis 1 cm. represented 1 treatment; the first wet measurement was plotted 0.5 cm. from the origin, the first dry measurement 1 cm., the second wet measurement 1.5 cm. etc., as is shown in the figure. The upper 5 points (wet measurements) were then connected by a line and the lower 5 points by another line. An area was thus enclosed, that was larger the greater the shrinkage of the leather; this area was then measured with a planimeter. Values were recorded for the following: A_5 = total area in square millimeters; A_3 = total area for only 3 immersions; A_{+3} = area above the 10 cm. ordinate line, corresponding to leather expansion; A_{-3} = area below the 10 cm. ordinate line, corresponding to shrinkage; W_{max} = maximum length, and S_{max} = maximum shrinkage or shortest length found in any measurement, each expressed as per cent of the original length of 10 cm. The accompanying diagram shows 2 such charts or plots (not to exact scale) and the A values.

During immersion for 24 hours in the sweat solution, there is some leaching of tannin or other substances from the leather. A trial was made of dipping the leather in the sweat solution only until it was saturated, then storing the moist leather at 35°C for 24 hours. This method caused less shrinkage than the regular procedure. Repeated immersion in water caused little shrinkage. Many commercial insole leathers were tested by the above described method and certain relations were found, although in general there was little relation between shrinkage behavior and chemical analysis. Leather high in fat shrunk less than that low in fat. High solubles reduced shrinkage somewhat, probably because



the buffering action of the soluble matter opposed the change to an alkaline condition caused by decomposed sweat. Location in the hide affected shrinkage behvaior. A_s values (averages from tests on a number of leathers) were 257, 345 and 442 for leather from bend, neck and flank locations respectively. Bend leather often shrank little on the first or second immersion, but as much as leather from from the neck area on the fourth and fifth immersions. Thin leathers shrank more rapidly and to a greater degree than thick leathers. Thick, tight leather had the greatest resistance to shrinkage. Old process, pit tanned leather (A_s = 287) was little better than modern rapid tanned leather (A_s = 279)

Type of hide, whteher dry or green salted, did not affect shrinkage. Many leathers, mostly of modern tannage, shrank badly (A_5 = 296-616), but this behavior could not be related to raw material or the tanning process.

The behavior of leather tanned with a single vegetable tannin or a syntan were tested by dividing a double bend into 18 × 22 centimeter pieces and tanning them with various materials for two months in a vat with liquors strengthened to 7°Be. The materials and results are shown in the following table:

Tannnig material	A_5	A_{-5}	A_3	S_{max}	Appearance after treatment
Sulfited quebracho	212	152	96	−2.0	dark brown, flexible, flat
Wattle	270	222	96	−4.5	black, hard, slightly curled
Chestnut	292	288	100	−7.0	black, hard, slightly curled
Myrobalans	396	376	136	−9.0	black, hard, badly curled
Spruce	516	408	232	−6.5	black, hard, curled
Lignintan SU72	720	708	300	−9.0	brown, hard, badly curled
Tanicor HGR	132	84	60	−1.5	light brown, flexible, flat
Tanigan NR	276	224	132	−4.0	dark brown, stiff, flat
Tanigan extra Q	372	352	176	−5.0	light brown, hard, curled
Tanigan extra B	404	404	172	−7.5	red brown, hard, badly curled
Basyntan extra K	428	340	196	−5.5	black, hard, curled

The vegetable tannins are in the order found for other properties, such as affinity for skin and shrink temperature. Tanicor HGR (which has a resorcin base) was better than quebracho; the other syntans were like an average vegetable tannin. Further experiments were made with a standard mixture containing equal parts of tannin from wattle, oakwood, chestnut, spruce and Tanicor HGR, and in which various pretreatments were tried. No effect on shrinkage behavior was found from pretanning with quinone, formaldehyde or Coriagen, pretreating with tan liquor or using anionic wetting agents during tanning. Improvement of insoles by pre- or post-tanning with either chrome or alum has been reported. A vegetable tanned leather (A_5 = 348) after tanning with Chromitan B had the following shrinkage (A_5) values: Pretanning with 1 per cent Cr_2O_3, 316; with 2.5 per cent Cr_2O_3, 256; retanning with 1 per cent Cr_2O_3, 268; with 2.5 per cent, 212. Chrome improved the sweat resistance greatly, but alum improved it even more, as is shown by the following A_5 values: vegetable leather used for the retanning, 272; retanning with Alutan O (2.5 per cent Al_2O_3), 168; with Blancotan B, (2.5 per cent Al_2O_3), 160; with Casella 34138, (either 1 per cent or 2.5 per cent Al_2O_3), 124; either pre- or re-tanning with a combination of Chromitan B (1 per cent Cr_2O_3) and Alutan O (2.5 per cent Al_2O_3), 136; pretanning with Chromitan B (1 per cent Cr_2O_3), then retanning with Alutan O (2.5 per cent Al_2O_3), 120. The fact that different aluminum compounds differ appreciably in their effect shows that the way the metal is fixed in the complex is important. It is known that chrome and also alum react with vegetable tannins. The increased stability to alkaline sweat of a combination mineral-vegetable tanned leather is partly caused by the fixation of the vegetable tannin, but the tanning action of the mineral tan also plays an important role. Fixing agents, such as hexamethylenetetramine (Asulgan) did not improve resistance; the precipitate which they form with vegetable tannin is soluble in ammonia. Cationic wetting agents, which form precipitates with vegetable tannins that are insoluble in ammonia, definitely improved shrinkage behavior. A marked improvement was found by retanning vegetable leather (A_5 = 272) with amphoteric or cationic tannins, which tan and also fix vegetable tannins. A_5 values of 152- 204 were found for the Baykanols R52, SR52 and

S52. Tannin 34291 (Casella Mainkur) produced the lowest A_5 value, 104, found in this work. The results as a whole show that even poor leathers shrink little on the first or second treatments, repeated treatment with sweat solution is necessary to evaluate insole behavior. Shrinkage is not a property of the original leather, but is a result of damage by sweat, practically always alkaline sweat. This relation between increase in pH value and damage indicates that damage is the result of a loosening of the bond between tannin and hide substance. The increasingly detanned leather then shows increasing differences in length between the wet and dry condition. Astringent tans are therefore better than those with weak affinity for skin. Soluble loading materials resist detanning, and also delay the pH rise that causes loosening of the tannin. Whether the tannin is washed from the leather or remains unfixed between the leather fibers is not important as regards damage, but in the latter case, there is a darkening and hardening characteristic of sweat damaged insoles. The problem of producing a stable insole lies in finding a tannin or tannin combination that will make leather stable in the alkaline range. Chrome tanned leather is relatively stable to alkali but swells when moist. The fact that the water unstable alum tannage equals or excels chrome tannage and that both are much better as retans than as pretans shows, that in addition to a mineral tannage as such, there is also a pronounced fixing action on the vegetable tannin. In this respect the newer cationic and amphoteric tannins resemble mineral tanning agents. I. D. C.

Leather and Tanning Agents. IX. The Application of Plastics in Sole Leather Manufacture. By H. Batzer. *Das Leder* **5**, 5 (1954). A review of the use of polymerization, polycondensation, and polyaddition plastics in sole leather to improve resistance to wear and water. I. D. C.

After-Treatment of Sole Leather. By O. Grimm. *Das Leder* **5**, 1 (1951). A review of various methods of treating leather to increase its resistance to water and to wear. The methods include loading with tannin or other materials, fixing the tannin, and impregnation. I. D. C.

Hide and Skin Markets of the World. By W. Freudenberg. *Das Leder* **4**, 14, 58, 85, 111, 136, 155, 250, 304 (1953). A description of the kinds, numbers, quality, and grades of hides and skins produced in Africa. (A revision of the section on hides and skins in Handbuch der Gerbereichemie und Lederfabrikation, W. Grassman, Editor; to be used in the new edition to appear about 1956). I. D. C.

PATENTS

Leather Water Repellent. U. S. Pat. 2,672,455. C. C. Currie, Midland, Mich., assignor to Dow Corning Corp. Appl. Aug. 4, 1952. As a composition of matter, a mixture comprising (1) 15 to 50 per cent by weight of a titanium compound selected from the group consisting of titanium compounds having the general formula $Ti(OR)_4$ and aliphatic hydrocarbon soluble partial hydrolyzates thereof in which compounds R is selected from the group consisting of aliphatic hydrocarbon radicals of less than 13 carbon atoms and hydroxylated aliphatic hydrocarbon radicals of less than 13 carbon atoms and containing less than 4 hydroxy radicals; (2) 5 to 70 per cent by weight of a methyl polysiloxane copolymer composed of trimethylsiloxane units and SiO_2 units, said units being in such proportion that the ratio of methyl radicals to silicon atoms is from 1.0:1 to 2.5:1; and

(3) 15 to 80 per cent by weight of a polysiloxane having the general formula

$$R'_nSiO_{\frac{4-n}{2}}$$

where R′ is a radical selected from the group consisting of alkyl and alkylene radicals of less than 4 carbon atoms, and monocyclicaryl radicals, and n has an average value of 2 to 2.9, each silicon atom in said polysiloxane (3) having at least one of the defined hydrocarbon radicals attached thereto.

Method of Making a Composite Sole Leather and Product. U. S. Pat. 2,673,171. L. Bellavoine, Paris, France. Appl. May 10, 1951. A method of making a composite sole leather which comprises juxtaposing and securing together an external leather layer, an internal leather layer and an intermediate layer of a flexible material impervious to liquids, and boring the composite layer to form a multiplicity of substantially wedge-shaped holes extending through the internal and intermediate layers and into the external layer to a distance from the outer face thereof, the intermediate layer being made of an elasticity such that the holes formed therein retract to very small dimensions such that the liquids cannot flow therethrough.

Making Leather. B. Pat. 639,616. American Cyanamid Co. Nov. 18, 1947. Light-resistant white chrome tanned leather is obtained by impregnating chrome tanned leather with an aromatic sulfonated tanning agent and with a water-soluble methylol melamine. The said tanning agent may be a disulfodinaphthylmethane formed by condensing two molecules of a naphthalene sulfonic acid with one molecule of formaldehyde or a formaldehyde condensation product of a sulfonated phenol or cresol. While the neutralized product, desirably having a *p*H 6 to 8, is preferred, the alkaline or acid form may be used. The methylol melamine should remain water soluble in the presence of salt (NaCl), e.g. trimethylol melamine the preparation of which is given. The methylol melamine is usually applied after the aromatic sulfonate tanning agent, but it may be applied simultaneously therewith or even prior thereto. In the example, low-grade cowhides are chrome tanned in the presence of sodium chloride, neutralized with $NaHCO_3$, washed with water, treated with a 3 per cent solution of a disulfodinaphthylmethane of *p*H 6 to 8, washed and treated with 3.5 per cent of trimethylol melamine in aqueous solution, washed and fat liquored with 5 per cent sulfonated vegetable oil, 1 per cent neatsfoot oil and 4 per cent titanium dioxide.

Leather Substitutes. B. Pat. 640,245. J. Seraphim. Aug. 28, 1946. Sheets of substitute hide are prepared by immersing textile fibres in an aqueous vinyl resin emulsion plasticized by casein, gluten or an organic phthalate, e. g. dimethyl glycol phthalate. One or both sides of the sheet may afterwards be coated with the same or another plasticized vinyl resin emulsion which may also contain a caustic reagent, e.g. caustic soda and ammonia. A filler and/or a pigment, e.g. lithopone may be included.

Stretching Leather. B. Pat. 640,545. O. Hallen. Jan. 19, 1948. A machine for working leather glove blanks.

Leather Washing Machine. B. Pat. 643,359. A washing machine for cleansing hides comprises a vat or like container in which the hides are to be cleansed, rotatably mounted,

above floor level, about a horizontal axis and provided internally with a paddle rotatable about a horizontal axis which is spaced from the vat axis and mechanism for rotating the paddle to agitate the vat contents during a cleansing operation and for rotating or tilting the vat, as and when the cleansing operation is completed, so as to discharge said contents toward the floor.

Liming Skins and Hides. B. P. 643,452. S. Payno. Oct. 14, 1946. Hides and skins are treated prior to tanning but subsequently to dehairing, in an aqueous medium containing only lime and a neutral alkali metal or magnesium salt, or a mixture of said salts, said salt or mixtures thereof, having a solubility at substantially room temperature less than that of the corresponding calcium salt. The neutral salts may be sodium, potassium or magnesium, chlorides or nitrates. The aqueous medium, which is saturated with respect to the lime and contains at least 0.6 per cent thereof, is employed at the rate of 100—600 per cent (preferably 100—150 per cent) of the weight of the skins or hides and contains 0.1 to 0.8 per cent of the neutral salt or mixtures thereof.

Tanning. B. P. 644,451. L. Bolgar. Nov. 19, 1947. A soluble synthetic tanning agent is prepared by condensing sulfonic acids with a compound which contains in the molecule an active methylol group and an amino group and which has been made by condensing urea or thiourea with ammonia and an aldehyde in acid medium. Urea-aldehyde or phenol-aldehyde resins not containing sulfonic groups may be included in the reaction mixture. The products may be neutralized wholly or partly with ammonia, caustic soda, $Al(OH)_3$ $Cr(OH)_3$ or by buffering, and may be used in combination with vegetable, aluminum or chrome tanning. Specified are sulfonic acids of naphthalene, alkyl-naphthalenes and lignin.

Artificial Leather. B. P. 644,855. J. Seraphim. Aug. 28, 1946. Artificial leather or hide is produced by treating leather waste with rubber latex containing also aluminum sulfate, sodium hypo-sulfite, casein, an organic acid and ammonia in the proportions of 15 to 30 kilograms leather to 6 to 15 kilograms rubber latex containing 60 per cent of solid ingredients in a solution of 100 to 300 litres of water. The proportions of the solid ingredients in the solution are 1.5 to 4 kilograms sodium hyposulfite, 0.3 to 0.5 kilograms casein, 0.15 to 0.40 kilograms acid (e.g. oxalic acid), 1.3 to 4 kilograms aluminum sulfate and 500 to 1000 cc. of ammonia. The solution is mixed with the leather scrap, kneaded and allowed to stand, while the water drains away, and then compressed and dried.

Artificial Leather. B. P. 644,856. J. Seraphim. Aug. 28, 1946. Artificial leather is prepared by treating the usual fibrous support with the usual emulsion containing xanthate and/or an ethenoid resin and/or latex and also containing an aqueous solution of urea together with gluten or casein or amylaceous material. The emulsion may also contain an organic solvent, e.g. alcohol and a plasticizer. Specified impregnating compositions, in grams, are (1) 20 to 40 urea, 15 to 35 gluten or casein, 80 to 150 xanthate of cellulose and sodium, 30 to 60 ethenoid resin, 35 to 70 plasticizer and 40 to 100 water; and (2) 60 to 100 urea, 200 to 320 water, 90 to 150 gluten, 150 to 350 alcohol, 15 to 20 ethenoid resin and 10 to 35 plasticizer.

Degreasing Skins. B. P. 645,040. S. Friestedt. July 19, 1948. Pickled sheep and goat skins, after liming and puering, are degreased by placing them in an ammonia bath of such strength that, after the pickle acid has been neutralized, the bath remains alkaline

and the excess ammonia reacts with that part of the fat which has been saponified during the liming to form soluble ammonia soaps. Preferably the skins remain in this soap solution for a sufficient time to emulsify any unsaponified fat. Skins are pickled by drumming for 1 hour in hydrochloric or sulphuric acid containing common salt and drained. The pickled skins are drummed with a solution of 3 per cent concentrated ammonia in 400 per cent water (based on pickled skin weight) for ½—3 hours at 92—100°F. and then dried. If necessary, the dried skins are treated with ammonia again or drummed with varnoline at 125—135°F. for 20—30 minutes with subsequent removing of varnoline by putting out or centrifuging and washing with running water. The skins may be repickled after treatment. Other fat-dissolving agents such as trichlorethylene or kerosene may be used in place of varnoline, and emulsifying agents may be added.

Leather Making. B. P. 648,236. E. G. Wilson. Dec. 30, 1948. A method of tanning leather consists in immersing the leather in a tanning liquor, causing the leather to follow a travel path in which it is guided over and around appropriately positioned rollers whereby it is bent repeatedly from end to end, first in one direction and then in the opposite direction, and between each bending is supported in an unflexed position on or by conveyor bands, or their equivalents, arranged to move between the said rollers, for controlled periods of time.

Artificial Leather. B. P. 648,331. A. Kemp and Underfelts, Ltd. Dec. 12, 1947. Imitation leather is made by preparing a substantially electrically neutral aqueous suspension of finely-divided particles of rubber by adding to rubber latex an aqueous emulsion of rubber particles carrying a positive electric charge, mixing the resultant suspension with a dilute aqueous suspension of mineral, or preponderantly mineral fibres, e.g. asbestos fibres which may be dyed, and forming the mixture into a sheet. Vulcanizing agents may be added and the mix after flocculation poured on to a gauze, e.g. of 40—60 mesh per square inch and the excess moisture removed under vacuum to form sheets.

Synthetic Tanning Agent. B. P. 649,516. L. Bolgar. Apr. 1, 1947. A synthetic tanning agent is made by condensing a sulfonic acid of a novolak prepared from phenol, cresol, their homologues or naphthols, with a compound which contains in the molecule an active methylol group and an amino group and which is made by reacting urea and/or thiourea and ammonia together with an aldehyde in acid solution. In an example, a compound which has the probable formula:

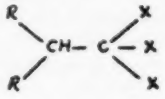
$$OH—CH_2—NH—CO—NH—CH_2—NH—CO—NH—CH_2—NH_2+\tfrac{1}{4}H_2SO_4$$

is prepared by mixing formaldehyde solution, aqueous ammonia and sulphuric acid, heating to 70°C., adding urea solution gradually and continuing heating. The product is then reacted in the presence of formic acid with a product obtained by sulfonation of a novolate prepared by reacting, in acid medium, phenol and formaldehyde in the approximate molar ratio of 2 : 1. More formic acid is then added. As a modification, phenols, phenolic resins, lignin sulfonic acids or other sulfonic acids may be admixed with the novolak sulfonic acid starting material. The products may be used, in the free state, buffered, or as their ammonium, sodium, chromium or aluminum salts to which formic or oxalic acid may be added.

Leather Making. B. P. 649,570. L. Bolgar. Apr. 1, 1947. A synthetic tanning agent is made by condensing β-naphthol sulfonic acid with a compound which contains an active

methylol group and an amino group and has been made from urea and/or thiourea and ammonia condensed together with an aldehyde in acid solution. The β-naphthol sulfonic acid may be admixed with phenols, phenolic resins and lignin sulfonic acids or with another aromatic sulfonic acid. The agents may be neutralized or buffered or used as ammonium, sodium, chromium, aluminum or magnesium salts, or basic salts, which may be mixed with weak or medium strong acids such as formic or oxalic acids. The products may be used at *p*H values of 5—6.

Proofing Materials Against Insects. B. P. 650,403. Geigy Co., H. T. Fergusson, and R. Williamson. June 7, 1948. Textile and other fibrous materials are protected from attack by insects or rendered unsuitable as a habitation for them by treatment with an aqueous dispersion containing an insecticide of the general formula.



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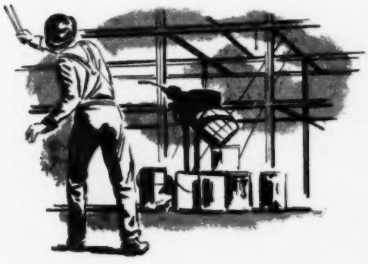

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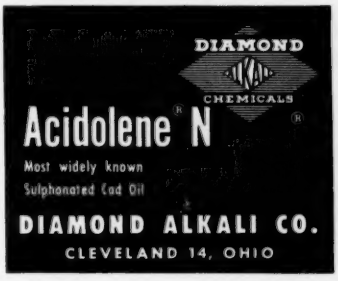

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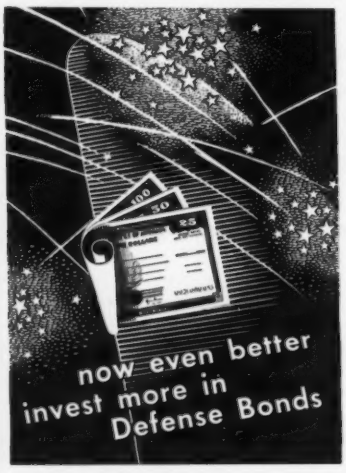

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INDEX TO ADVERTISERS

AMERICAN CYANAMID COMPANY V
AMERICAN DYEWOOD CO. X
AMERICAN EXTRACT CO. ..... Outside Back Cover
APEX CHEMICAL CO., INC. XXIV
ARKANSAS COMPANY, INC. VI
ARMOUR LEATHER CO. XXXV
ARTHUR C. TRASK CO. XXXI
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XVI
BARIUM REDUCTION CORPORATION XXV
BARKEY IMPORTING CO., INC. ..... VII—XIX
BONA ALLEN, INC. XXXIII
BORNE SCRYMSER COMPANY IX
BUCKMAN LABORATORIES, INC. XVII
CHEMTAN COMPANY XXI
CLINTON FOODS XXXVI
DIAMOND ALKALI CO. XXXI
EISENDRATH TANNING CO. XXVII
FRANK F. MARSHALL XXXI
GARDEN STATE TANNING INC. XXXI
GENERAL DYESTUFF CORPORATION IX
HOOKER ELECTROCHEMICAL CO. XVIII
HOWES LEATHER CO., INC. XXXIII
INTERNATIONAL PRODUCTS CORP. XII
KEPEC CHEMICAL CORPORATION XXXI
LEATHER AND SHOES XXXII
LEATHER MANUFACTURER, THE XXIX
L. H. LINCOLN & SON, INC. XXXVII
MARDEN WILD CORPORATION XXVI
MEAD CORPORATION, THE XIII
NEWARK LEATHER FINISH CO. XXXIII
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXVII
OLSON SALES AGENCY, THE ..... Inside Front Cover
PACIFIC COAST BORAX CO. XXVIII
PENNIMAN & BROWNE, INC. XXXVI
PRESTO COLOR CO. XXVIII
REILLY-WHITEMAN-WALTON CO. XXIX
RIVER PLATE CORPORATION, THE XIV
ROBESON PROCESS CO. II
ROHM & HAAS IV
SALEM OIL & GREASE CO. XXX
SAXE CUTCH CORPORATION XXVI
SHOE & LEATHER REPORTER XXX
SOCONY-VACUUM OIL CO. I
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XI
SOUTH AFRICAN WATTLE EXTRACT MFRS. ASSO. XV
SUN OIL COMPANY XXVI
TANEXCO, INC. ..... XLII—Inside Back Cover
TANIMEX CORPORATION ..... XXXV—XXXIX
TANNERS' COUNCIL RESEARCH LABORATORY ..... XXXVI—XL
TEAS EXTRACT CO. III
UNION STARCH & REFINING CO. XXXIV
UNITED STATES RUBBER COMPANY XXXVIII
WALLERSTEIN COMPANY, INC. XXIV
WARNER CO. XXVII
WHITTEMORE-WRIGHT CO. XXVIII
WOLF, JACQUES & CO. VIII
YOUNG CO., J. S. XX

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